

Table 2. Hydrogen-bonding geometry (Å, °)

| D—H...A                     | D—H   | H...A | D...A     | D—H...A |
|-----------------------------|-------|-------|-----------|---------|
| O1—H1...O51 <sup>i</sup>    | 0.850 | 1.933 | 2.681 (2) | 146.2   |
| O1—H2...O1W <sup>ii</sup>   | 0.850 | 2.005 | 2.852 (2) | 174.4   |
| O2—H4...O12 <sup>iii</sup>  | 0.850 | 1.951 | 2.739 (2) | 153.8   |
| O2—H3...O1W <sup>iv</sup>   | 0.850 | 1.824 | 2.627 (2) | 156.9   |
| O3—H5...O52 <sup>ii</sup>   | 0.850 | 1.766 | 2.601 (2) | 167.2   |
| O3—H6...O2W <sup>v</sup>    | 0.850 | 1.826 | 2.666 (3) | 169.4   |
| O4—H7...O51 <sup>v</sup>    | 0.850 | 2.132 | 2.852 (3) | 142.2   |
| O4—H8...O2W <sup>v</sup>    | 0.850 | 2.452 | 2.994 (3) | 122.3   |
| O1W—H1W...O31 <sup>vi</sup> | 0.850 | 2.124 | 2.910 (2) | 153.6   |
| O1W—H2W...O52               | 0.850 | 1.829 | 2.643 (3) | 159.7   |
| O2W—H3W...O2 <sup>vii</sup> | 0.850 | 2.118 | 2.887 (3) | 150.2   |
| O2W—H4W...O32               | 0.850 | 1.848 | 2.682 (3) | 166.6   |

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

H atoms were found in difference Fourier maps and then placed in geometrically optimized positions with  $d(\text{O—H}) = 0.85 \text{ \AA}$  and  $d(\text{C—H}) = 0.96 \text{ \AA}$ . They were then allowed to ride with isotropic displacement parameters 20% greater than those of the atoms to which they were attached. A final difference map revealed the largest residual peak of  $+1.1 \text{ e \AA}^{-3}$  to be located *ca*  $0.9 \text{ \AA}$  from O2, the terminal aqua ligand of the Cu atom. This could be refined using disordered positions for this atom with an improvement of *ca* 0.2% in discrepancy indices. The minor component of O2, labelled O2', forms a different hydrogen-bond arrangement. It still occupies a geometrically reasonable position about the square-pyramidal Cu<sup>II</sup> since it has different deviations from orthogonality to the other ligands than does O2. Using common linked displacement parameters, the occupancy factors of O2 and O2' refined to 92.5 and 7.5%, respectively. These were then fixed and O2 refined anisotropically and O2' isotropically without restraints.

Data collection: XSCANS (Siemens, 1994a). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XP (Siemens, 1994b).

The Research Grants Council of Hong Kong is gratefully acknowledged for support of this work (grants HKUST205/93E and 6148/97P).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1164). Services for accessing these data are described at the back of the journal.

## References

- Cambridge Structural Database (1997). Version 6. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
- Chui, S. S.-Y. & Williams, I. D. (1999). *J. Chem. Soc. Dalton Trans.* Submitted.
- Guerrero, P., Casellato, U., Ajo, D., Sitran, S., Vigato, P. A. & Graziani, R. (1988). *Inorg. Chim. Acta*, **142**, 305–308.
- Khodashova, T. S., Porai-Koshits, M. A., Davidenko, N. K. & Vilasova, N. N. (1984). *Koord. Khim.* **10**, 262–265.
- Pech, R. & Pickardt, J. (1988). *Acta Cryst.* **C44**, 992–994.
- Robl, C. (1988). *Z. Anorg. Allg. Chem.* **561**, 57–65.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994a). *XSCANS User's Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994b). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Yaghi, O. M. & Li, H. (1995). *Nature*, **378**, 703–706.

Ye, B., Mak, T., Williams, I. D. & Li, X. Y. (1997). *Chem. Commun.* pp. 1813–1814.

*Acta Cryst.* (1999). **C55**, 196–198

## The homoleptic lithium complex

### [Li(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub>

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(Received 14 November 1997; accepted 15 September 1998)

## Abstract

The homoleptic lithium acetonitrile complex tetra(acetonitrile-*N*)lithium perchlorate, [Li(CH<sub>3</sub>CN)<sub>4</sub>]ClO<sub>4</sub>, was synthesized by the reaction of LiClO<sub>4</sub> and acetonitrile. The structural measurements are more regular than those of two homoleptic analogues reported previously by others.

## Comment

A large number of homoleptic [M(CH<sub>3</sub>CN)<sub>m</sub>] cationic complexes ( $m = 2$ –6) are known for both monovalent and divalent metals. Anions for such complexes have included Cl<sup>-</sup>, I<sup>-</sup>, [MCl<sub>4</sub>]<sup>-</sup> ( $M = \text{B, Al, Ga, In, Tl, Fe}$ ), [MBr<sub>4</sub>]<sup>-</sup> ( $M = \text{Al, Fe, In, Tl}$ ), [MF<sub>4</sub>]<sup>-</sup> ( $M = \text{Sb, Sn}$ ), [MF<sub>6</sub>]<sup>x-</sup> ( $M = \text{Bi, Sb}$ ), ClO<sub>4</sub><sup>-</sup>, [WF<sub>7</sub>]<sup>-</sup>, [Sn(NCS)<sub>6</sub>]<sup>2-</sup>, [Cu<sub>2</sub>I<sub>3</sub>]<sup>-</sup>, [W<sub>4</sub>N<sub>4</sub>CCl<sub>14</sub>]<sup>-</sup>, and [Bi<sub>4</sub>Cl<sub>16</sub>]<sup>4-</sup>. Cationic complexes of transition metals of the form [M<sub>2</sub>(CH<sub>3</sub>CN)<sub>10</sub>]<sup>4+</sup> have also been synthesized wherein the counter-ion is [BF<sub>4</sub>]<sup>-</sup> (Brokaar *et al.*, 1970; Reedijk & Groeneveld, 1968; Zuur & Groeneveld, 1967). Among the Li complexes reported to date, only two have been characterized by X-ray crystal structure analysis, namely, [Li(CH<sub>3</sub>CN)<sub>4</sub>]I (Raston *et al.*, 1989), which diffracted poorly, was disordered and gave limited data, and [Li(CH<sub>3</sub>CN)<sub>4</sub>][Cu<sub>2</sub>I<sub>3</sub>] (Hoyer & Hartl, 1992). During the course of investigating the

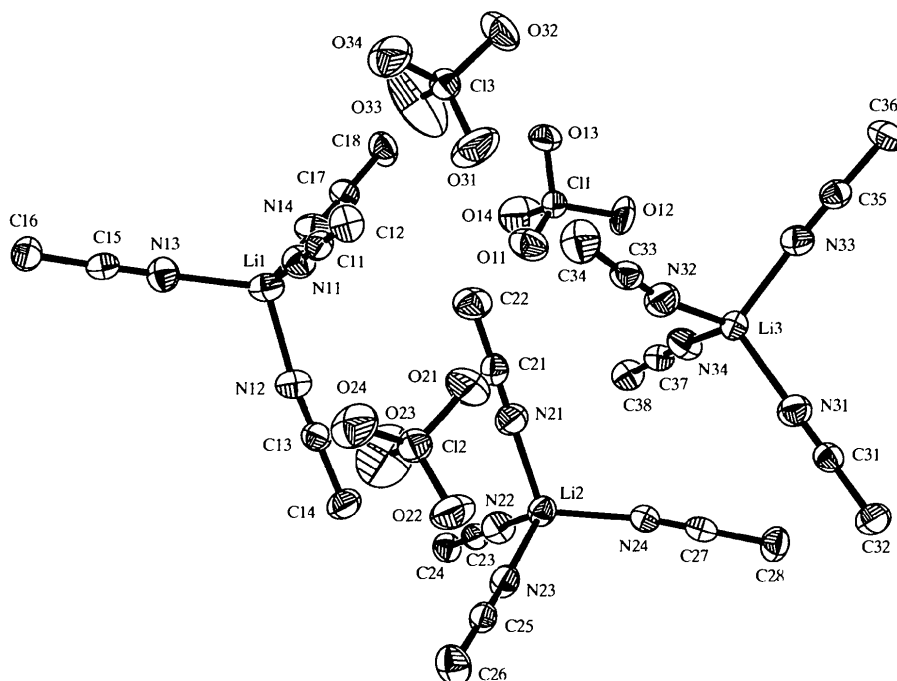


Fig. 1. The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level.

synthesis of Li complexes of tridentate ether ligands (Yokota & Verkade, 1999), we obtained crystals of  $[\text{Li}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ , (I). Here, we compare our structural results with those reported for  $[\text{Li}(\text{CH}_3\text{CN})_4]\text{I}$  and  $[\text{Li}(\text{CH}_3\text{CN})_4][\text{Cu}_2\text{I}_3]$ .

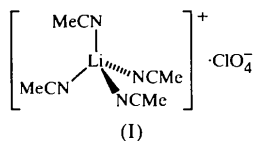


Fig. 1 shows the three different  $[\text{Li}(\text{CH}_3\text{CN})_4]^+$  and  $\text{ClO}_4^-$  ions present in the asymmetric unit of (I). In the  $[\text{Li}(\text{CH}_3\text{CN})_4]^+$  cation, the metal is tetrahedrally coordinated by four  $\text{CH}_3\text{CN}$  molecules. All Li—N distances are equal within  $3\sigma$  [ $2.025(16) \text{ \AA}$ ], and this is also true of the N—Li—N angles [ $109(2)^\circ$ ]. In  $[\text{Li}(\text{CH}_3\text{CN})_4]\text{I}$ , one of the four Li—N distances is rather short [ $1.73(7) \text{ \AA}$ ], and the N—Li—N angles vary considerably [ $96(2)$ ,  $98(3)$ ,  $105(3)$  and  $119(3)^\circ$ ; Raston *et al.*, 1989]. These data are suspect, however, in view of the disorder problems referred to above. In  $[\text{Li}(\text{CH}_3\text{CN})_4][\text{Cu}_2\text{I}_3]$  (Hoyer & Hartl, 1992), the N—Li—N angles are also rather unequal [ $102(2)$ ,  $109(2)$ ,  $111(2)$  and  $112(2)^\circ$ ]. Although the Li—N distances are very similar in (I), the Li—N—C angles are slightly bent (average  $172.6^\circ$ ), as is also the case in  $[\text{Li}(\text{CH}_3\text{CN})_4][\text{Cu}_2\text{I}_3]$ .

## Experimental

A solution of  $\text{LiClO}_4$  (1.60 g, 15.0 mmol) in acetonitrile (5 ml), maintained at 278 K for 24 h, provided colorless crystals of (I) [0.98 g, 24% yield; m.p. 315–316 K;  $^1\text{H NMR}$  (acetone- $d_6$ ):  $\delta$  2.30 (*s, br*)]. The crystalline material undergoes rapid evaporative decomposition at room temperature, which made it difficult to mount a crystal for data collection. A specimen with the approximate dimensions of a 0.2 mm sphere was mounted in a drop of oil on the end of a glass capillary.

### Crystal data

$[\text{Li}(\text{C}_2\text{H}_3\text{N})_4]\text{ClO}_4$

$M_r = 270.61$

Orthorhombic

$Pna2_1$

$a = 24.1291(3) \text{ \AA}$

$b = 8.4281(1) \text{ \AA}$

$c = 20.6083(3) \text{ \AA}$

$V = 4190.96(9) \text{ \AA}^3$

$Z = 12$

$D_x = 1.287 \text{ Mg m}^{-3}$

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 7172

reflections

$\theta = 1.69\text{--}27.50^\circ$

$\mu = 0.283 \text{ mm}^{-1}$

$T = 173(2) \text{ K}$

Spheroid

$0.2 \times 0.2 \times 0.2 \text{ mm}$

Colorless

### Data collection

Siemens SMART CCD

diffractometer

$\omega$  scans

Absorption correction:

multi-scan (Blessing,

1995)

$T_{\min} = 0.817$ ,  $T_{\max} = 0.946$

35 976 measured reflections

9513 independent reflections

7196 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 27.5^\circ$

$h = 0 \rightarrow 31$

$k = 0 \rightarrow 10$

$l = -26 \rightarrow 26$

## Refinement

|   |  |
|---|--|
| Refinement on $F^2$                               | $\Delta\rho_{\max} = 0.281 \text{ e } \text{\AA}^{-3}$   |
| $R[F^2 > 2\sigma(F^2)] = 0.057$                   | $\Delta\rho_{\min} = -0.265 \text{ e } \text{\AA}^{-3}$  |
| $wR(F^2) = 0.116$                                 | Extinction correction:                                   |
| $S = 1.053$                                       | <i>SHELXTL</i> (Siemens, 1994a)                          |
| 9513 reflections                                  | Extinction coefficient:                                  |
| 501 parameters                                    | 0.00164 (14)   |
| Only coordinates of H atoms refined               | Scattering factors from                                  |
| $w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 2.7861P]$ | <i>International Tables for Crystallography</i> (Vol. C) |
| where $P = (F_o^2 + 2F_c^2)/3$                    | Absolute structure:                                      |
| $(\Delta/\sigma)_{\max} = 0.006$                  | Flack (1983)   |
|   | Flack parameter = 0.23 (8)                               |

All H atoms were treated as riding, with relative isotropic displacement parameters. The less-than-optimum mounting contributed to an unexpectedly large spread in the transmission coefficients.

Data collection: *SMART* (Siemens, 1994b). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1994a). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

The authors are grateful to the National Science Foundation for a grant in support of this research. The structure was originally determined at the Iowa State Molecular Structure Laboratory. A second data collection was completed on a Siemens SMART CCD diffractometer, to obtain a better quality structure. Final refinements were completed at the X-ray Crystallographic Facility at the University of Minnesota.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1013). Services for accessing these data are described at the back of the journal.

## References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.  
 Brokaar, G., Groeneveld, W. L. & Reedijk, J. (1970). *Recl Trav. Chim. Pays-Bas*, **89**, 1117–1120.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Hoyer, M. & Hartl, H. (1992). *Z. Anorg. Allg. Chem.* **612**, 45–50.  
 Raston, C. L., Whitaker, C. L. & White, A. H. (1989). *Aust. J. Chem.* **42**, 201–207.  
 Reedijk, J. & Groeneveld, W. L. (1968). *Recl Trav. Chim. Pays-Bas*, **87**, 513–527.  
 Siemens (1994a). *SHELXTL*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Siemens (1994b). *SMART Software Reference Manual*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Siemens (1995). *SAINT Software Reference Manual*. Version 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Yokota, Y. & Verkade, J. G. (1999). *Polyhedron*. Submitted.  
 Zuur, A. P. & Groeneveld, W. L. (1967). *Recl Trav. Chim. Pays-Bas*, **86**, 1089–1102.

*Acta Cryst.* (1999). **C55**, 198–200

## Samarium 3,5-dinitrobenzoate dihydrate

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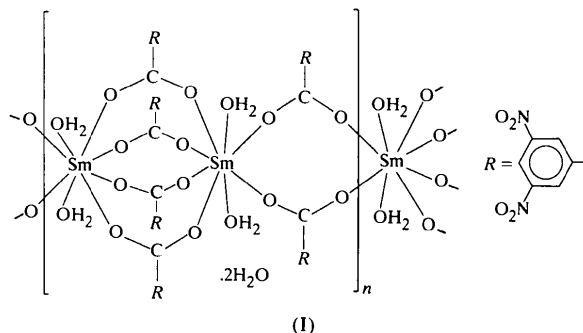
(Received 10 March 1998; accepted 28 September 1998)

## Abstract

The coordination around the Sm atom in the title compound, catena-poly[[[tetraqua-1κ<sup>2</sup>O,2κ<sup>2</sup>O-tetrakis(μ-3,5-dinitrobenzoato-O:O')disamarium]-bis(μ-3,5-dinitrobenzoato-O:O')] dihydrate], [Sm<sub>2</sub>(C<sub>7</sub>H<sub>3</sub>N<sub>2</sub>O<sub>6</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>].2H<sub>2</sub>O, is eightfold. The irregular square-antiprism coordination of the Sm ion is provided by six O atoms from six carboxylate groups and two water O atoms. The Sm ions are bridged alternately by four and two ligands, resulting in linear polymeric chains with two different Sm···Sm distances of 4.2476 (7) and 5.0831 (8) Å, and Sm—O distances in the range 2.355 (4)–2.559 (4) Å. A set of hydrogen bonds exists between the nitro groups and the water molecules.

## Comment

Rare earth carboxylates have been reported to show chelating, bridging and chelating–bridging modes of coordination which can be simultaneous or separate (Ma *et al.*, 1994; Hiyalov *et al.*, 1981; Bats *et al.*, 1979; Moore *et al.*, 1971; Tahir *et al.*, 1996). The title compound, (I), was synthesized in order to study the structure of Sm–carboxylate and to find out the mode of coordination around Sm. As can be seen from Fig. 1, the coor-



dination around the Sm ion is eightfold, involving six carboxylate O atoms [O1, O3, O5, O2<sup>ii</sup>, O4<sup>ii</sup> and O6<sup>i</sup>; symmetry codes: (i)  $-x, -y, 1-z$ ; (ii)  $1-x, -y, 1-z$ ] and two water O atoms (O7 and O8). In the coordination sphere, the shortest bond length [2.355 (4) Å] is