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### Bis[2-(2-ethoxyethyl)-*N,N,N',N'*-tetraethylmalondiamide-*O*<sup>1</sup>,*O*<sup>3</sup>]tris(nitrato-*O,O'*)-lanthanum(III)

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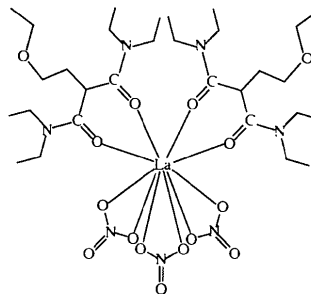
#### Abstract

2-(2-Ethoxyethyl)-*N,N,N',N'*-tetraethylmalondiamide (TEEEMA, C<sub>15</sub>H<sub>30</sub>N<sub>2</sub>O<sub>3</sub>) reacts with lanthanum(III) nitrate to give the title complex, [La(NO<sub>3</sub>)<sub>3</sub>(TEEEMA)<sub>2</sub>], in which the two carboxyl functions of each TEEEMA ligand are bonded to the metal ion together with three bidentate nitrate ions. This structure establishes that the ether O atom of the central chain of TEEEMA is not bonded to the metal ion, at least in the solid state. The coordination environment geometry is different from that of the lanthanum complex of *N,N,N',N'*-tetraethylmalondiamide (TEMA).

#### Comment

In the course of studies related to nuclear fuel reprocessing, malondiamides have been proposed as extractants able to separate actinides(III) from the majority of fission products, with the exception of lanthanides(III) which are co-extracted with actinides(III) (Cuillerdier *et al.*, 1991). Extensive data have been compiled so as to understand the extraction mechanisms (Nigond, 1992; Nigond *et al.*, 1994; Madic & Hudson, 1998). The first step in such investigations is the determination of the nature of the complex species which are formed (stoichiometry, structure and nature of bonding). The optimization of a suitable extractant for this process

was undertaken and a large number of molecules with the general formula *RR'N—CO—CHR''—CO—NRR'* was evaluated (Madic & Hudson, 1998). Malondiamides with *R''* = C<sub>2</sub>H<sub>4</sub>OC<sub>n</sub>H<sub>2n+1</sub> are molecules of interest because they lead to higher extraction of both actinides(III) and lanthanides(III). In order to explain this behaviour, the participation in complexation of the ether O atom present in the *R''* radical was suggested, but no structural evidence was available. The present study of the title complex, (I), deals with a ligand which belongs to this family and contributes to the elucidation of the last point.



(I)

Some crystal structures of complexes formed by malondiamide derivatives, *e.g.* *N,N,N',N'*-tetramethyl-, *N,N,N',N'*-tetraethyl-, *N,N'*-dicyclohexyl-*N,N'*-dimethyl- and *N,N'*-dimethyl-*N,N'*-diphenylmalondiamide, with lanthanides (La<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Er<sup>3+</sup> and Yb<sup>3+</sup>) have been determined (Castellano & Becker, 1981; Byers *et al.*, 1994; Chan *et al.*, 1997; Den Auwer *et al.*, 1999). The malondiamide/metal ion stoichiometry of the complexes formed is 1:1 or 2:1 when the three counter-ions are bonding (NO<sub>3</sub><sup>-</sup>), whereas it is 4:1 or even 5:1 when the counter-ions are non-bonding (PF<sub>6</sub><sup>-</sup>). In most cases, the malondiamide is bidentate, so that the metal ion coordination number is between 8 and 10. Some solid-state and solution EXAFS (Extended X-ray Absorption Fine Structure) measurements have also been performed recently (Den Auwer *et al.*, 1999). In the case of the La<sup>3+</sup> complex of *N,N,N',N'*-tetraethylmalondiamide (TEMA), the two ligands are roughly coplanar, two nitrate ions being located on each side and the third one crossing this plane (Byers *et al.*, 1994). The present ligand, TEEEMA, differs from TEMA by the presence of a -(CH<sub>2</sub>)<sub>2</sub>-O-CH<sub>2</sub>CH<sub>3</sub> ether chain on the central methylenic C atom. The complex formed with La<sup>3+</sup> has the same 2:1 stoichiometry as the TEMA complex, with three bidentate nitrate ions. The ether O atoms are not bonded to the metal ion, the ether chains being stretched away from the complex core. The La—O<sub>TEEEMA</sub> distances [mean value 2.52 (2) Å], as well as the La—O<sub>nitrate</sub> distances [mean value 2.64 (3) Å], are in agreement with those already found [mean values 2.53 (5) and 2.70 (8) Å, respectively]. However, the

geometry of the coordination polyhedron is different from that of the TEMA complex, as well as from those of the other  $\text{Ln}(\text{NO}_3)_3(\text{malondiamide})_2$  complexes. The carboxyl O atoms of the two TEEEMA molecules, which are not coplanar, are located in one half of the coordination sphere, the three nitrate ions being located in the other half. The present geometry prevents the ether chains being too close to the nitrate ions, as would occur if the geometry was the same as that of the TEMA complex. The geometry of the malondiamides can be described by the torsion angles within the molecule (Chan *et al.*, 1997). As in the structures reported previously, all the  $\text{C}_{\text{ext}}-\text{N}-\text{C}-\text{C}$  angles (where  $\text{C}_{\text{ext}}$  is the first C atom of a terminal alkyl chain bonded to nitrogen) are close to ideal values, *i.e.* 180 or  $0^\circ$ . The  $\text{N}-\text{C}-\text{C}-\text{C}$  torsion angles involving the two carboxyl C atoms range, in absolute value, from 110 to  $144^\circ$ , which is the usual range. Finally, the  $\text{O}=\text{C}\cdots\text{C}=\text{O}$  torsion angles, which characterize the degree of planarity of the central bonding core, are  $28.8(2)$  and  $-19.5(2)^\circ$  for the two TEEEMA molecules, which indicates a slight deviation from planarity, as in the complexes reported previously. The overall geometry can be viewed as being derived from that of a bicapped dodecahedron, however strongly distorted (Drew, 1977). It can be concluded that the unusual complex geometry and the presence of the central chain do not induce a malondiamide conformation much different from the one currently observed in trivalent lanthanide complexes. Furthermore, the ether O atom of the central substituent has been shown not to be involved in complexation, at least in the solid state, which leaves open the question of the extraction enhancement observed in such compounds.

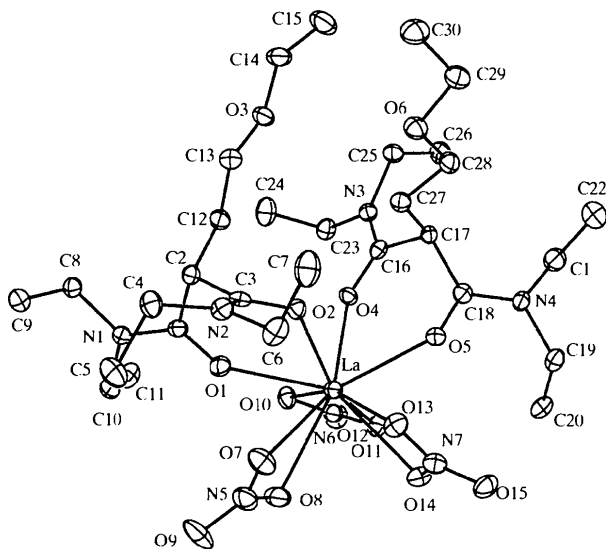


Fig. 1. The title molecule with the atom-numbering scheme. H atoms have been omitted for clarity and displacement ellipsoids are drawn at the 40% probability level.

## Experimental

TEEEMA was provided by Panchim, Lisses (91), France, and used without further purification. TEEEMA (0.7 mmol) was reacted with  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.35 mmol) in ethanol (10 ml). The resulting product was then recrystallized from methanol/acetone (1:1).

### Crystal data

$[\text{La}(\text{NO}_3)_3(\text{C}_{15}\text{H}_{30}\text{N}_2\text{O}_3)_2]$   
 $M_r = 897.76$   
 Monoclinic  
 $P2_1/n$   
 $a = 11.2868(6) \text{ \AA}$   
 $b = 30.877(2) \text{ \AA}$   
 $c = 11.9177(6) \text{ \AA}$   
 $\beta = 92.746(3)^\circ$   
 $V = 4149(2) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.437 \text{ Mg m}^{-3}$   
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 17 990 reflections  
 $\theta = 2.16\text{--}25.91^\circ$   
 $\mu = 1.100 \text{ mm}^{-1}$   
 $T = 123(2) \text{ K}$   
 Parallelepiped  
 $0.35 \times 0.25 \times 0.20 \text{ mm}$   
 Colourless

### Data collection

Nonius Kappa-CCD diffractometer  
 $\varphi$  rotation scans with  $2^\circ$  steps  
 Absorption correction: empirical (MULABS in PLATON; Spek, 1998)  
 $T_{\text{min}} = 0.63$ ,  $T_{\text{max}} = 0.73$   
 17 990 measured reflections  
 5396 independent reflections

4512 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.042$   
 $\theta_{\text{max}} = 25.91^\circ$   
 $h = 0 \rightarrow 13$   
 $k = 0 \rightarrow 32$   
 $l = -14 \rightarrow 14$   
 Intensity decay: none

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.076$   
 $S = 1.060$   
 5294 reflections  
 480 parameters  
 H atoms constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 10.6890P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = -0.002$   
 $\Delta\rho_{\text{max}} = 0.414 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.834 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

La—O1	2.512(3)	La—O8	2.611(3)
La—O2	2.507(3)	La—O10	2.661(3)
La—O4	2.544(3)	La—O11	2.606(3)
La—O5	2.514(3)	La—O13	2.692(3)
La—O7	2.649(3)	La—O14	2.617(3)
O1—La—O2	67.47(10)	O7—La—O8	48.50(11)
O2—La—O4	83.91(10)	O10—La—O11	48.60(10)
O4—La—O5	66.22(10)	O13—La—O14	48.22(10)
O5—La—O1	141.35(10)		

Data collection: *Kappa-CCD Software* (Nonius, 1997). Cell refinement: *HKL* (Otwinowski & Minor, 1997). Data reduction: *HKL*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1046). Services for accessing these data are described at the back of the journal.

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## Bis[ $\mu$ -2,2',2''-nitrilotriethanethiolato(2-)-N,S,S':S']dinickel(II)

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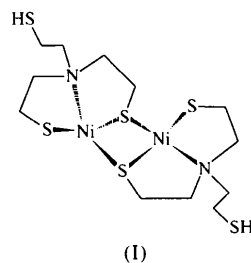
## Abstract

The neutral dimeric title complex, [Ni<sub>2</sub>(C<sub>6</sub>H<sub>13</sub>NS<sub>3</sub>)<sub>2</sub>], has crystallographic twofold symmetry and two square-planar NiS<sub>3</sub>N planes hinged through a pair of bridging thiolate S atoms, with a folding angle of 110.84(6)°. The thiol group of each ligand is pendant and links

molecules in chains through weak S—H···S hydrogen bonds.

## Comment

The title compound, (I), a neutral dimeric complex, has been prepared previously (Colpas *et al.*, 1990) and by analogy was assumed to have a structure similar to that of the dimeric complex of nickel with the ligand bis(2-mercaptoethyl)[2-(methylthio)ethyl]amine. We confirm here this assumption and show the presence of two pendant thiol groups.



The X-ray analysis of (I) shows the dimeric complex to consist of two square-planar NiS<sub>3</sub>N units hinged together through a pair of bridging thiolate S atoms (Fig. 1). The two halves are related by a crystallographic twofold axis. Therefore, the N and one thiolate S atom of each ligand are bonded to a single Ni atom, the second thiolate S atom bridges the two Ni atoms, and the thiol arm is pendant and forms rather weak S—H···S hydrogen bonds to link the molecules in sheets parallel to the *bc* plane.

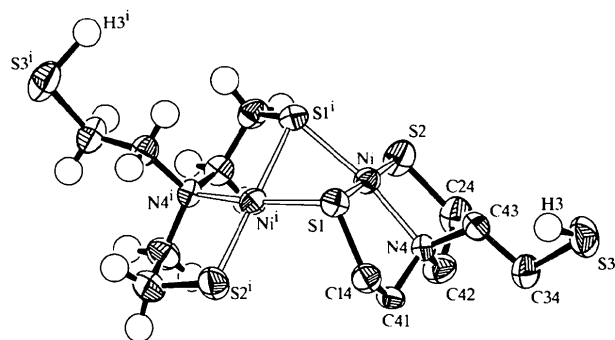


Fig. 1. A view of the title compound showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms are shown with an arbitrary radius and H atoms in one half of the molecule have been omitted for clarity. The molecule lies across a crystallographic twofold axis. [Symmetry code: (i)  $\frac{1}{2} - x, y, -z$ .]

The angle between the normals to the two NS<sub>3</sub> mean planes is 107.47(6)°. The folding angle, defined by Colpas *et al.* (1990) as the angle between the normals to the intersecting NiS<sub>2</sub> planes, is 110.84(6)°. These