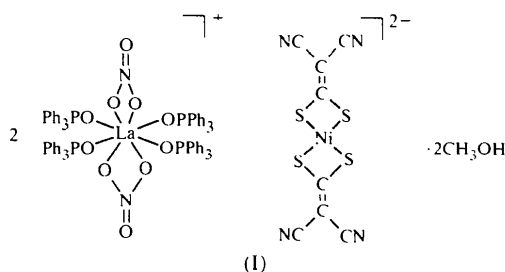


## References

- Amos, R. D., Handy, N. C., Jones, P. G., Kirby, A. J., Parker, J. K., Percy, J. M. & Su, M. D. (1992). *J. Chem. Soc. Perkin Trans. 2*, pp. 549–556.
- Chan, V. Y., Clark, C. I., Giordano, J., Green, A. J., Karalis, A. & White, J. M. (1996). *J. Org. Chem.* **61**, 5227–5233.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Gable, R. W., Hoskins, B. F., Linden, A., McDonald, I. A. S. & Steen, R. J. (1994). *Process.data. Program for the Processing of CAD-4 Diffractometer Data*. University of Melbourne, Australia.
- Green, A. J., Kuan, Y. & White, J. M. (1995). *J. Org. Chem.* **60**, 2734–2738.
- Issa, W., Green, A. J. & White, J. M. (1997). *Aust. J. Chem.* **50**, 927–932.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. University of Cambridge, England.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- White, J. M. (1995). *Aust. J. Chem.* **48**, 1227–1251.
- White, J. M. & Robertson, G. B. (1992). *J. Org. Chem.* **57**, 4638–4644.
- Zsolnai, L. (1994). *ZORTEP. An Interactive ORTEP Program*. University of Heidelberg, Germany.

## Comment

In our previous papers dealing with metal complexes of the isomaleonitriledithiolate (i-mnt) ligand, we reported the mononuclear complexes (Bu<sub>4</sub>N)<sub>2</sub>[Zn(i-mnt)<sub>2</sub>], (Et<sub>4</sub>N)<sub>2</sub>[Pd(i-mnt)<sub>2</sub>] (Long *et al.*, 1996) and [Pd(Ph<sub>3</sub>P)<sub>2</sub>(i-mnt)] (Long *et al.*, 1997), and a mixed-metal cluster compound (Et<sub>4</sub>N)<sub>2</sub>[PdWS<sub>4</sub>(i-mnt)] (Long *et al.*, 1997). Recently, by employing sodium ions half-capped by crown ethers as bridges, we obtained the one-dimensional coordination polymers [{(benzo-15-crown-5)Na}<sub>2</sub>M(i-mnt)<sub>2</sub>]<sub>n</sub>, where M is Pd (Long, Chen *et al.*, 1998) or Ni (Long, Cui *et al.*, 1998). In an attempt to construct coordination polymers using La<sup>III</sup> ions as bridges, we produced the title ionic complex [La(NO<sub>3</sub>)<sub>2</sub>(Ph<sub>3</sub>PO)<sub>4</sub>]<sub>2</sub>[Ni(i-mnt)<sub>2</sub>]·2CH<sub>3</sub>OH, (I).



*Acta Cryst.* (1999). **C55**, 1662–1664

**[La(NO<sub>3</sub>)<sub>2</sub>(Ph<sub>3</sub>PO)<sub>4</sub>]<sub>2</sub>[Ni(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]<sub>2</sub>·2CH<sub>3</sub>OH**

DE-LIANG LONG, HUAI-MIN HU, JIU-TONG CHEN AND JIN-SHUN HUANG

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, People's Republic of China. E-mail: hjs@ms.fjirm.ac.cn

(Received 21 December 1998; accepted 11 May 1999)

## Abstract

The title compound, bis(nitrato-*O,O'*)tetrakis(triphenylphosphine oxide-*O*)lanthanum(III)(1+)-bis(1,1-dimercaptoethylene-2,2-dithiolato-*S,S'*)nickelate(II)(2-)-methanol (2/1/2), consists of discrete [La(Ph<sub>3</sub>PO)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup> cations, [Ni(C<sub>4</sub>N<sub>2</sub>S<sub>2</sub>)<sub>2</sub>]<sup>2-</sup> anions and methanol solvent molecules. In the planar anion, the Ni<sup>II</sup> atom is located on an inversion center and is coordinated symmetrically by two bidentate isomaleonitriledithiolate ligands through their S atoms. In the cation, the lanthanum(III) center is linked to eight O atoms, four of which are from four different triphenylphosphine oxide ligands and four are from two bidentate nitrate groups chelating the lanthanum(III) center on each side of the approximate plane defined by the four Ph<sub>3</sub>PO ligands.

As shown in Fig. 1, complex (I) consists of discrete [La(OPPh<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and [Ni(i-mnt)<sub>2</sub>]<sup>2-</sup> ions; there are no short cation–anion contacts. All the atoms in the anion are coplanar to within 0.1 Å. The nickel(II) center lies on a crystallographic inversion center and is symmetrically coordinated by two bidentate isomaleonitriledithiolate ligands through their S atoms [Ni—S 2.2043 (12) and 2.2236 (12) Å]. The conformation of the i-mnt ligand is similar to that found in [{(benzo-15-crown-5)Na}<sub>2</sub>Ni(i-mnt)<sub>2</sub>]<sub>n</sub>·nCH<sub>2</sub>Cl<sub>2</sub> and [Ni(NH<sub>3</sub>)<sub>4</sub>]-Ni(i-mnt)<sub>2</sub>] (Zhu *et al.*, 1995). Within each cation, the La<sup>III</sup> atom is coordinated by eight O atoms; four of these are derived from four triphenylphosphine oxide ligands and form an approximate plane. Two bidentate nitrate groups chelate the lanthanum(III) center on each side of the plane of the four Ph<sub>3</sub>PO ligands. The coordination polyhedron around the La<sup>III</sup> atom is irregular, with the main distortion being caused by the presence of the small bidentate nitrate groups, but it can still be described as a dodecahedron, with the two trapezia defined by O1/O12/O11/O4 and O2/O3/O21/O22 intersecting at an angle of 90.3 (1)°. Wang *et al.* (1989) reported a six-coordinated Ph<sub>3</sub>PO–lanthanum complex, [La(Ph<sub>3</sub>PO)<sub>5</sub>-Cl][FeCl<sub>4</sub>]<sub>2</sub>, whilst a nine-coordinated example, [La(Ph<sub>3</sub>PO)<sub>3</sub>(NO<sub>3</sub>)<sub>3</sub>], was identified by Huang *et al.* (1987). The title compound has P=O, La—O(Ph<sub>3</sub>PO) and La—O(NO<sub>3</sub>) bond distances comparable with those found in the complexes reported earlier, although their coordination polyhedra are quite different.

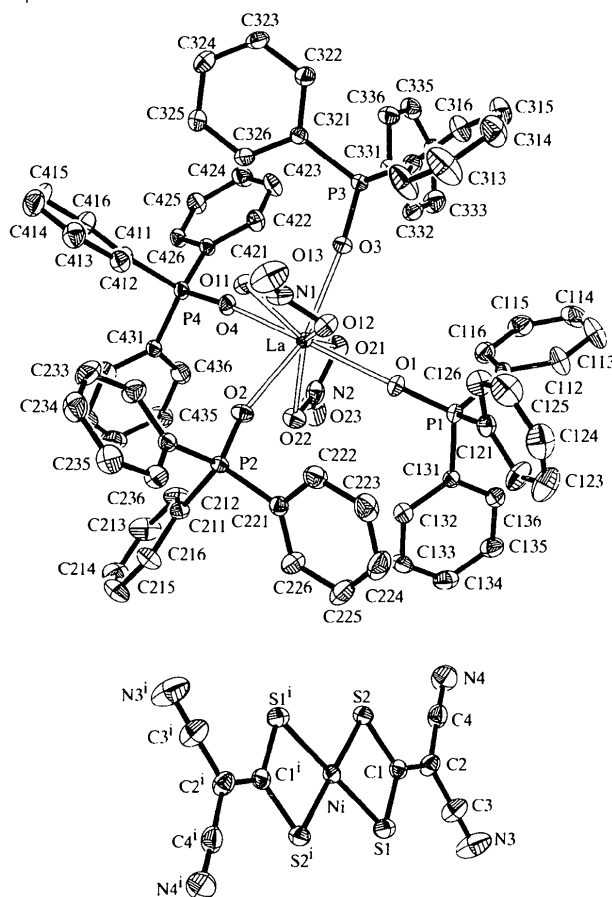


Fig. 1. The structure of the title molecule (*SHELXTL*; Siemens, 1994*b*). The methanol solvent molecules and the H atoms have been omitted for clarity. [Symmetry code: (i)  $1-x, -1-y, -z$ .]

## Experimental

A solution of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.12 g, 0.5 mmol) in methanol (20 ml) was added with stirring to solid sodium isomaleonitriledithiolate [ $\text{Na}_2(\text{i-mnt})$ ; 0.20 g, 1.0 mmol]. This mixture was then mixed with another solution prepared from  $\text{Ph}_3\text{PO}$  (0.84 g, 3 mmol) and  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.43 g, 1.0 mol) in methanol (20 ml). After filtration, the resulting solution was reduced to a volume of about 15 ml, from which black crystals were obtained. Crystals suitable for X-ray diffraction were obtained from this solution by slow evaporation in air. IR spectrum (KBr pellet,  $\text{cm}^{-1}$ ): 2199 [*s*,  $\nu(\text{C}\equiv\text{N})$ ], 1491 [*s*], 1471 [*s*,  $\nu(\text{C}=\text{C}, \text{Ph})$ ], 1437 [*vs*,  $\nu(\text{C}=\text{C}, \text{i-mnt})$ ], 1144 [*vs*], 1122 [*vs*,  $\nu(\text{P}=\text{O})$ ], 1083 [*s*,  $\nu(\text{P}-\text{C})$ ], 1026 [*m*,  $\nu(\text{C}-\text{S})$ ].

## Crystal data

$[\text{La}(\text{NO}_3)_2(\text{C}_{18}\text{H}_{15}\text{OP})_4]_2 \cdot$   
 $[\text{Ni}(\text{C}_4\text{N}_2\text{S}_2)_2] \cdot 2\text{CH}_3\text{O}$   
 $M_r = 3155.18$   
 Triclinic  
 $P\bar{1}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 6759  
 reflections  
 $\theta = 1.50\text{--}23.23^\circ$

$a = 14.8435(3) \text{ \AA}$   
 $b = 14.8573(2) \text{ \AA}$   
 $c = 18.9784(4) \text{ \AA}$   
 $\alpha = 107.983(1)^\circ$   
 $\beta = 96.779(1)^\circ$   
 $\gamma = 103.117(1)^\circ$   
 $V = 3796.3(2) \text{ \AA}^3$   
 $Z = 1$   
 $D_x = 1.380 \text{ Mg m}^{-3}$   
 $D_m$  not measured

$\mu = 0.882 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
 Block  
 $0.50 \times 0.35 \times 0.30 \text{ mm}$   
 Black

## Data collection

Siemens SMART CCD  
 diffractometer  
 $\omega$  scans  
 Absorption correction:  
 empirical (*SADABS*;  
 Sheldrick, 1996)  
 $T_{\text{min}} = 0.649, T_{\text{max}} = 0.768$   
 14 995 measured reflections  
 10 619 independent  
 reflections

8204 reflections with  
 $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.028$   
 $\theta_{\text{max}} = 23.23^\circ$   
 $h = -16 \rightarrow 16$   
 $k = -16 \rightarrow 13$   
 $l = -18 \rightarrow 21$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.085$   
 $S = 0.971$   
 10 619 reflections  
 900 parameters  
 H atoms constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0348P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.80 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for*  
*Crystallography* (Vol. C)

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

La—O1	2.399(2)	O1—P1	1.507(3)
La—O2	2.400(3)	O2—P2	1.506(3)
La—O3	2.425(2)	O3—P3	1.508(3)
La—O4	2.394(2)	O4—P4	1.517(3)
La—O11	2.612(3)	Ni—S1	2.2236(12)
La—O12	2.577(3)	Ni—S2	2.2043(12)
La—O21	2.638(3)	S1—C1	1.733(4)
La—O22	2.579(3)	S2—C1	1.715(4)
N1—O11	1.271(4)	C1—C2	1.382(6)
N1—O12	1.274(4)	C2—C4	1.415(7)
N1—O13	1.217(4)	C2—C3	1.416(7)
N2—O21	1.272(4)	C3—N3	1.152(6)
N2—O22	1.255(4)	C4—N4	1.146(6)
N2—O23	1.221(4)		
O1—La—O2	100.23(9)	O4—La—O3	86.31(9)
O1—La—O3	94.49(9)	S2'—Ni—S2	180.00(6)
O2—La—O3	151.67(9)	S2'—Ni—S1'	78.07(4)
O4—La—O1	154.26(9)	S2—Ni—S1'	101.93(4)
O4—La—O2	90.59(9)	S2—Ni—S1	78.07(4)

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

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1994*a*). Program(s) used to solve structure: *SHELXTL* (Siemens, 1994*b*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

This research was supported by grants from the National Natural Science Foundation of China and the Natural Science Foundation of Fujian Province.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1312). Services for accessing these data are described at the back of the journal.

## References

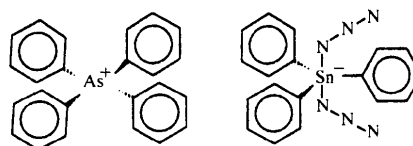
- Huang, C., Xu, R., Zhou, Y. & Xu, G. (1987). *Acta Physicochim. Sin.* **3**, 491–500.
- Long, D.-L., Chen, J.-T., Cui, Y. & Huang, J.-S. (1998). *Chem. Lett.* pp. 171–172.
- Long, D.-L., Cui, Y., Chen, J.-T., Cheng, W.-D. & Huang, J.-S. (1998). *Polyhedron*, **17**, 3969–3975.
- Long, D.-L., Hou, H.-W., Xin, X.-Q., Luo, B.-S., Chen, L.-R. & Yu, K.-B. (1996). *J. Coord. Chem.* **38**, 15–24.
- Long, D.-L., Zheng, H.-G., Xin, X.-Q., Sake, G. & Shibahara, T. (1997). *Polyhedron*, **16**, 4305–4311.
- Sheldrick, G. M. (1996). *SADABS. Program for Absorption Correction*. University of Göttingen, Germany.
- Siemens (1994a). *SAINT Software Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994b). *SHELXTL. Structure Determination Programs. Version 5*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1996). *SMART Software Reference Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wang, H.-K., Zhang, M.-J. & Jing, X.-Y. (1989). *Inorg. Chim. Acta*, **163**, 19–23.
- Zhu, R., Lu, S., Huang, X., Wu, Q., Yu, R. & Huang, J. (1995). *Acta Cryst.* **C51**, 1515–1517.

around the metal ion, with the azide moieties in axial positions having equal bond distances [Sn—N 2.278 (5) and 2.281 (6) Å] but different bond angles [Sn—N—N 117.4 (4) and 125.2 (5)°] to the tin. The cation has its usual tetrahedral geometry.

## Comment

Previously, we synthesized and characterized by Mössbauer and vibrational spectroscopy tetraphenylarsonium and tetramethylammonium salts of the complex anions [Ph<sub>3</sub>Sn(N<sub>3</sub>)<sub>2</sub>]<sup>−</sup>, [Ph<sub>3</sub>Sn(N<sub>3</sub>)(NCS)]<sup>−</sup>, [Me<sub>2</sub>Sn(N<sub>3</sub>)<sub>4</sub>]<sup>2−</sup> and [Ph<sub>2</sub>Sn(N<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub>]<sup>2−</sup> (Barbieri *et al.*, 1975). Trigonal-bipyramidal structures have been suggested for Ph<sub>3</sub>Sn<sup>IV</sup> with apical pseudohalide ligands, while for the R<sub>2</sub>Sn<sup>IV</sup> derivatives, *trans* octahedral geometries have been assumed (R = Me, Ph).

The X-ray structure determination of [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P]<sub>2</sub>[Sn(N<sub>3</sub>)<sub>4</sub>Me<sub>2</sub>] (Halfpenny, 1995) confirmed the Mössbauer results for the octahedral geometry, while the trigonal-bipyramidal structure with the azide groups in axial positions has been found in the X-ray structures of piperidinium and quinuclidinium [Ph<sub>3</sub>Sn(N<sub>3</sub>)<sub>2</sub>] (Wharf *et al.*, 1997). In the latter, the azide groups are not equivalent, with different Sn—N bond distances due to hydrogen-bond interactions with the cations. These results indicated that a compound without protonated cations should provide interesting information. Accordingly, we now describe the X-ray structure of the title compound, (I).



(I)

The anion has the expected trigonal-bipyramidal coordination geometry around the Sn atom, with the azide ligands in axial positions and equivalent in their Sn—N and N—N bond lengths (Fig. 1 and Table 1). In fact, the Sn—N bond distances are equal and their values are intermediate between those found for asymmetric bonding in the protonated derivatives, which vary from 2.216 (3) to 2.396 (2) Å in the piperidinium salt and from 2.226 (4) to 2.371 (4) Å in the quinuclidinium salt (Wharf *et al.*, 1997). The azide ligands are coordinated with the difference in Sn—N—N angles probably resulting from packing requirements rather than from different resonance forms of the azide ligands because N<sub>α</sub>—N<sub>β</sub> and N<sub>β</sub>—N<sub>γ</sub> are the same in the two azide ligands. The present structure has no significant non-bonded contacts, the shortest is an intramolecular contact of 2.45 Å between N1 and H—C14 of the coordinated phenyl ligand, while the shortest interionic contact is N6<sup>⋯</sup>H40—C40

*Acta Cryst.* (1999). **C55**, 1664–1665

## Tetraphenylarsonium diazidotriphenylstannate

FRANCO BENETOLLO,<sup>a</sup> GABRIELLA BOMBIERI,<sup>b</sup> GIUSEPPE ALONZO<sup>c</sup> AND NUCCIO BERTAZZI<sup>d</sup>

<sup>a</sup>ICTIMA, CNR, 35127 Padova, Italy, <sup>b</sup>Istituto di Chimica Farmaceutica, Università di Milano, Viale Abruzzi 42, 20131 Milano, Italy, <sup>c</sup>Dipartimento ITAF – Sezione Chimica, Università di Palermo, Viale delle Scienze 13, 90128 Palermo, Italy, and <sup>d</sup>Dipartimento di Chimica Inorganica, Università di Palermo, Viale delle Scienze 13, 90128 Palermo, Italy. E-mail: benetollo@ictr04.ictr.pd.cnr.it

(Received 9 June 1999; accepted 30 June 1999)

## Abstract

The triphenyltin–azide anion of the title tetraphenylarsonium salt, [As(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>][Sn(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>(N<sub>3</sub>)<sub>2</sub>], shows approximately trigonal-bipyramidal coordination geometry