Refinement

Refinement on F^2
R = 0.039
wR = 0.108
S = 1.080
3858 reflections
247 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 4.7336P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.900$ e Å^{-3}
$\Delta\rho_{min} = -1.122$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Mo—O	1.734 (3)	Co—P1	2.1473 (13)
Mo—O2	2.042 (3)	Co—P3	2.1519 (13)
Mo—O1	2.054 (3)	Co—P2	2.1555 (13)
Mo—O3	2.171 (3)	P1—O1	1.525 (3)
Mo—Cl1	2.3384 (12)	P2—O2	1.521 (3)
Mo—Cl2	2.3384 (12)	P3—O3	1.514 (3)
O—Mo—O2	93.71 (14)	O3—Mo—Cl1	85.74 (9)
O—Mo—O1	92.96 (14)	O—Mo—Cl2	97.77 (12)
O2—Mo—O1	85.88 (12)	O2—Mo—Cl2	89.12 (9)
O—Mo—O3	172.54 (13)	O1—Mo—Cl2	168.44 (9)
O2—Mo—O3	81.16 (12)	O3—Mo—Cl2	87.62 (9)
O1—Mo—O3	81.32 (12)	Cl1—Mo—Cl2	92.46 (5)
O—Mo—Cl1	99.12 (12)	P1—Co—P3	89.40 (5)
O2—Mo—Cl1	166.73 (9)	P1—Co—P2	92.44 (5)
O1—Mo—Cl1	90.08 (9)	P3—Co—P2	90.33 (5)

All phosphite methyl groups were disordered and their C atoms were refined on U_{iso} and with an occupancy factor of 0.5. No disorder was resolved for the Cp ring atoms, but they display large torsional displacements. The largest difference map features lie close to Mo. H atoms were constrained with a riding model and with $U(H)$ fixed at 1.5 (Me) or 1.2 (Cp) times U_{eq} of the parent atom.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: ORTEX (McArdle, 1995). Software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1313). Services for accessing these data are described at the back of the journal.

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Trimethylgermylethyl p-nitrobenzoate†

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Abstract

The structure of the title compound, $C_{12}H_{17}GeNO_4$ or $[Ge(CH_3)_3(C_9H_8NO_4)]$, was determined as part of ongoing studies of the properties of esters substituted in the β position with group IV metal atoms. The conformation of the Ge—C—C—O moiety is gauche, the CH_2—O distance is 1.463 (3) Å, the average Ge—Me distance is 1.944 (3) Å and the Ge—CH_2 distance is 1.966 (3) Å.

Comment

As part of our general interest in the structural consequences of the σ–σ* interaction between the high-lying C—M σ-bonding orbital (M = Si, Ge, Sn) and the low-lying C—O σ*-antibonding orbital in esters, ethers and alcohols substituted in the β position with group IV metal atoms (White, 1995; White & Robertson 1992; Green et al., 1995; Chan et al., 1996), the structure of trimethylgermylethyl p-nitrobenzoate, (I), was deter-

† Metal–organic name: trimethyl(p-nitrobenzoyloxyethyl)germanium(IV).

mined at low temperature. Compound (I) was prepared in three steps according to the Scheme below.

(a) Zn/Et$_2$O
(b) Me$_3$Ge-Cl
(c) LiAlH$_4$/Et$_2$O
(d) p-NO$_2$Ph-COCl. pyridine

(I)
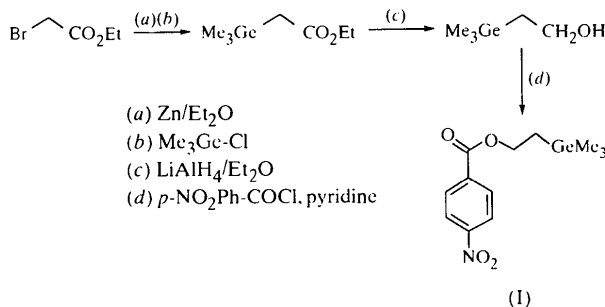
Compound (I) adopts a conformation in the solid state (Fig. 1) in which the Ge—C—C—O(PNB) (PNB is p-nitrobenzoate) dihedral angle is gauche [Ge—C1—C2—O1 = −51.2 (3)°]. As a result, overlap between the C2—Ge bonding orbital and the C2—O1 antibonding orbital is poor compared with the alternative antiperiplanar conformation. The C2—O1 bond distance [1.463 (3) Å] is not significantly different to that predicted for an unsubstituted primary C—O(PNB) distance (Amos et al., 1992). The corresponding silicon derivative adopts the antiperiplanar conformation in the solid state (Issa et al., 1997) and exhibits significant lengthening of the C—O(PNB) bond.
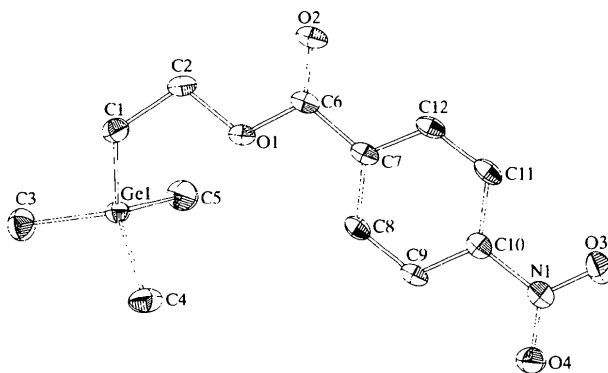

Fig. 1. ZORTEP (Zsolnai, 1994) diagram of (I). Displacement ellipsoids are at the 30% probability level.

Experimental

Colourless hexagonal plates of (I) (m.p. 332–333 K) bound by faces (100) (100) 0.32 mm, (110) (110) 0.25 mm, (110) (110) 0.25 mm and (001) (001) 0.018 mm, were grown from pentane.

Crystal data

[Ge(CH$_3$)$_3$(C$_9$H$_8$NO$_4$)]
M_r = 311.88
Monoclinic
$C2/c$
a = 12.670 (2) Å
b = 7.368 (1) Å
c = 29.704 (5) Å
β = 96.92 (1)°
V = 2752.7 (7) Å^3
Z = 8
D_x = 1.505 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54180 Å
Cell parameters from 25 reflections
θ = 25–30°
μ = 3.101 mm^{-1}
T = 130.0 (1) K
Plate
0.320 × 0.250 × 0.018 mm
Colourless

Data collection

Enraf–Nonius CAD-4S diffractometer
$\theta2\theta$ scans
Absorption correction:
Gaussian (Sheldrick, 1976)
T_{min} = 0.52, T_{max} = 0.94
3575 measured reflections
2251 independent reflections
2113 reflections with
$I > 2\sigma(I)$

R_{int} = 0.014
θ_{max} = 63.98°
h = −14 → 14
k = 0 → 8
l = 0 → 34
3 standard reflections
frequency: 160 min
intensity decay:
insignificant

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.085
S = 0.977
2248 reflections
232 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 5.0898P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.663 e Å^{-3}
$\Delta\rho_{min}$ = −0.444 e Å^{-3}
Extinction correction:
SHELXL97
Extinction coefficient:
6 (3) × 10^{-5}
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ge1—C4	1.941 (3)	Ge1—C1	1.966 (3)
Ge1—C5	1.945 (3)	O1—C2	1.463 (3)
Ge1—C3	1.946 (3)	C1—C2	1.508 (4)
C4—Ge1—C5	109.27 (14)	C5—Ge1—C1	111.74 (12)
C4—Ge1—C3	108.99 (14)	C3—Ge1—C1	107.38 (12)
C5—Ge1—C3	109.79 (14)	C2—C1—Ge1	116.1 (2)
C4—Ge1—C1	109.61 (12)	O1—C2—C1	107.9 (2)
C4—Ge1—C1—C2	94.3 (2)	C6—O1—C2—C1	−176.8 (2)
C5—Ge1—C1—C2	−27.0 (2)	Ge1—C1—C2—O1	−51.2 (3)
C3—Ge1—C1—C2	−147.5 (2)		

C—H distances are in the range 0.86 (3)–1.02 (5) Å.

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Data reduction: Process_data (Gable et al., 1994). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: ZORTEP (Zsolnai, 1994).

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Comment

In our previous papers dealing with metal complexes of the isomaleonitriledithiolate (i-mnt) ligand, we reported the mononuclear complexes $(Bu_4N)_2[Zn(i\text{-}mnt)_2]$, $(Et_4N)_2[Pd(i\text{-}mnt)_2]$ (Long *et al.*, 1996) and $[Pd(Ph_3P)_2(i\text{-}mnt)]$ (Long *et al.*, 1997), and a mixed-metal cluster compound $(Et_4N)_2[PdWS_4(i\text{-}mnt)]$ (Long *et al.*, 1997). Recently, by employing sodium ions half-capped by crown ethers as bridges, we obtained the one-dimensional coordination polymers $[\{(benzo\text{-}15\text{-}crown\text{-}5)Na\}_2M(i\text{-}mnt)_2]_n$, 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^{III} ions as bridges, we produced the title ionic complex $[La(NO_3)_2(Ph_3PO)_4]_2[Ni(i\text{-}mnt)_2]\cdot 2CH_3OH$, (I).

(I)
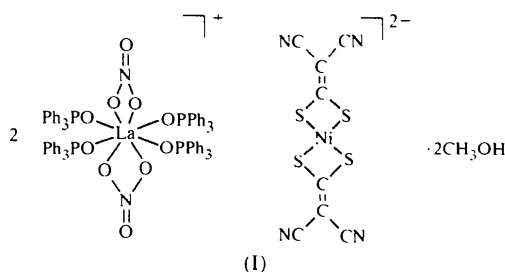
[La(NO₃)₂(Ph₃PO)₄]₂[Ni(C₄N₂S₂)₂]·2CH₃OH

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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 $[La(Ph_3PO)_4(NO_3)_2]^+$ cations, $[Ni(C_4N_2S_2)_2]^{2-}$ anions and methanol solvent molecules. In the planar anion, the Ni^{II} 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 Ph₃PO ligands.

As shown in Fig. 1, complex (I) consists of discrete $[La(OPPh_3)_4(NO_3)_2]^+$ and $[Ni(i\text{-}mnt)_2]^-$ 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 $[\{(benzo\text{-}15\text{-}crown\text{-}5)Na\}_2Ni(i\text{-}mnt)_2]_n\cdot nCH_2Cl_2$ and $[\{Ni(NH_3)_4\}Ni(i\text{-}mnt)_2]$ (Zhu *et al.*, 1995). Within each cation, the La^{III} 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 Ph₃PO ligands. The coordination polyhedron around the La^{III} 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 Ph₃PO–lanthanum complex, $[La(Ph_3PO)_5\text{-}Cl][FeCl_4]_2$, whilst a nine-coordinated example, $[La(Ph_3PO)_3(NO_3)_3]$, was identified by Huang *et al.* (1987). The title compound has P=O, La—O(Ph₃PO) and La—O(NO₃) bond distances comparable with those found in the complexes reported earlier, although their coordination polyhedra are quite different.