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Bis[$(\mu$ -2,6-diphenylphenoxido-*O*:*O*)diethylgallium]

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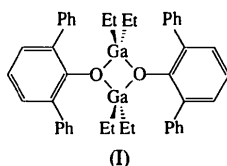
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Abstract

The title compound, $[\text{Ga}_2(\text{C}_{18}\text{H}_{13}\text{O})_2(\text{C}_2\text{H}_5)_4]$, contains discrete dimeric molecules containing an essentially planar four-membered (Ga—O—Ga—O) ring [O—Ga—O 75.04 (7) and 75.99 (7)°]. The Ga—O bond distances range from 1.992 (2) to 2.034 (2) Å and the O atoms have a trigonal-planar coordination.

Comment

There has been much interest in compounds of the alkylaluminium species with sterically bulky aryloxo ligands as reagents for new applications in organic synthesis and catalysis (Healy, Power & Barron, 1994). Some studies have been extended to gallium-containing molecules, with monomeric (Petrie, Olmstead & Power, 1991; Cleaver & Barron, 1993) and dimeric species having been reported. As part of a study on gallium-oxo species, we have studied the bulky 2,6-diphenylphenoxide ligand with the ethyl gallium residue. The four-membered ring found in the present dimeric compound, (I), has been found before, notably by Cleaver,



Barron, McGufey & Bott (1994), who reported seven derivatives with *tert*-butyl gallium.

The crystal structure of the title compound is found to contain discrete dimeric molecules containing a four-membered (Ga—O—Ga—O) ring (Fig. 1). The (Ga—O—Ga—O) ring is essentially planar [maximum deviation from the plane through the four atoms is 0.010 (1) Å], with smaller O—Ga—O ring angles [O—Ga—O 75.04 (7) and 75.99 (7)°] and correspondingly larger Ga—O—Ga angles than reported previously (Cleaver *et al.*, 1994). The Ga—O distances are in good agreement with earlier work on dimeric species (being longer than the monomeric values) and the geometry at the Ga atom is distorted tetrahedral (see Table 2). The Ga—C distances [1.961 (3)–1.971 (3) Å] are within the expected range (Hahn, Schneider & Reier, 1990).

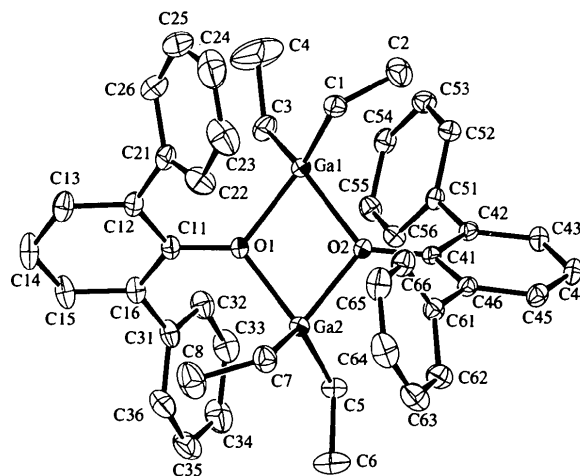


Fig. 1. The molecular structure of $[\text{Et}_2\text{Ga}(\text{OC}_{18}\text{H}_{13})]_2$ showing the labelling scheme, with displacement ellipsoids drawn at the 30% probability level. H atoms have been excluded for clarity.

The O atoms are in a trigonal-planar environment as has been noted before both in gallium-containing alkoxides (Cleaver *et al.*, 1994) and other μ_2 -alkoxides. The phenoxide C₆ rings are neither parallel nor perpendicular to the Ga₂O₂ ring, but make an average Ga—O—C—C torsion angle of -54° .

The title molecule has approximate *D*₂ point group symmetry.

Experimental

Working under argon, the title compound was prepared by slow addition of GaEt₃ (4.1 mmol) dissolved in toluene to a cold (210 K) solution of 2,6-diphenylphenol (4.1 mmol) in toluene. The solution was allowed to warm slowly to room temperature with stirring for 5 h. Removal of the volatiles gave the required product and colourless crystals were obtained from toluene.

Crystal data

[Ga₂(C₁₈H₁₃O)₂(C₂H₅)₄] $M_r = 746.29$

Triclinic

 $P1$ $a = 11.852(4) \text{ \AA}$ $b = 15.559(3) \text{ \AA}$ $c = 11.254(4) \text{ \AA}$ $\alpha = 98.30(2)^\circ$ $\beta = 115.70(3)^\circ$ $\gamma = 89.40(2)^\circ$ $V = 1847.2(10) \text{ \AA}^3$ $Z = 2$ $D_x = 1.342 \text{ Mg m}^{-3}$ D_m not measured

Data collection

Rigaku AFC-7S diffractometer

 $\omega/2\theta$ scans

Absorption correction:

 ψ scan (North, Phillips & Mathews, 1968) $T_{\min} = 0.42$, $T_{\max} = 0.59$

6854 measured reflections

6512 independent reflections

5489 observed reflections

 $[I > 2\sigma(I)]$

Refinement

Refinement on F^2 $R(F) = 0.0313$ $wR(F^2) = 0.0910$ $S = 0.985$

6512 reflections

476 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 1.6988P]$ where $P = (F_o^2 + 2F_c^2)/3$ Mo $K\alpha$ radiation $\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

 $\theta = 21.0\text{--}23.9^\circ$ $\mu = 1.491 \text{ mm}^{-1}$ $T = 150(2) \text{ K}$

Block

 $0.75 \times 0.40 \times 0.35 \text{ mm}$

Colourless

 $R_{\text{int}} = 0.0141$ $\theta_{\text{max}} = 25.01^\circ$ $h = 0 \rightarrow 14$ $k = -18 \rightarrow 18$ $l = -13 \rightarrow 12$

3 standard reflections

monitored every 150 reflections

intensity decay: 0.4%

 $(\Delta/\sigma)_{\text{max}} = 0.503$ $\Delta\rho_{\text{max}} = 0.747 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.585 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors

from *International Tables*for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and 6.1.1.4)

| | | | | |
|-----|-------------|--------------|-------------|-------------|
| C22 | -0.0054 (3) | 0.3860 (2) | 0.3208 (4) | 0.0522 (8) |
| C23 | 0.0001 (4) | 0.4752 (2) | 0.3240 (5) | 0.0725 (12) |
| C24 | -0.0523 (4) | 0.5094 (3) | 0.2102 (7) | 0.093 (2) |
| C25 | -0.1097 (4) | 0.4564 (4) | 0.0927 (6) | 0.106 (2) |
| C26 | -0.1159 (3) | 0.3657 (3) | 0.0863 (4) | 0.0775 (13) |
| C31 | 0.0834 (3) | 0.0215 (2) | 0.2663 (3) | 0.0379 (6) |
| C32 | 0.1422 (3) | -0.0036 (2) | 0.1839 (3) | 0.0425 (7) |
| C33 | 0.2187 (3) | -0.0735 (2) | 0.2060 (4) | 0.0533 (8) |
| C34 | 0.2387 (3) | -0.1182 (2) | 0.3104 (4) | 0.0632 (10) |
| C35 | 0.1822 (4) | -0.0934 (2) | 0.3934 (4) | 0.0621 (10) |
| C36 | 0.1051 (3) | -0.0243 (2) | 0.3709 (4) | 0.0512 (8) |
| C41 | 0.4808 (2) | 0.29108 (15) | 0.4322 (2) | 0.0250 (5) |
| C42 | 0.5487 (2) | 0.26364 (15) | 0.3587 (2) | 0.0271 (5) |
| C43 | 0.6772 (2) | 0.2856 (2) | 0.4143 (3) | 0.0341 (6) |
| C44 | 0.7401 (3) | 0.3316 (2) | 0.5421 (3) | 0.0373 (6) |
| C45 | 0.6729 (3) | 0.3584 (2) | 0.6135 (3) | 0.0339 (6) |
| C46 | 0.5435 (2) | 0.3403 (2) | 0.5601 (2) | 0.0275 (5) |
| C51 | 0.4906 (2) | 0.2097 (2) | 0.2241 (2) | 0.0274 (5) |
| C52 | 0.4873 (2) | 0.2419 (2) | 0.1133 (3) | 0.0331 (6) |
| C53 | 0.4455 (3) | 0.1892 (2) | -0.0096 (3) | 0.0371 (6) |
| C54 | 0.4079 (2) | 0.1031 (2) | -0.0234 (3) | 0.0354 (6) |
| C55 | 0.4100 (3) | 0.0703 (2) | 0.0856 (3) | 0.0363 (6) |
| C56 | 0.4495 (2) | 0.1236 (2) | 0.2076 (3) | 0.0322 (5) |
| C61 | 0.4787 (2) | 0.3772 (2) | 0.6423 (3) | 0.0319 (5) |
| C62 | 0.5159 (3) | 0.3571 (2) | 0.7703 (3) | 0.0425 (7) |
| C63 | 0.4656 (4) | 0.3991 (2) | 0.8532 (3) | 0.0549 (9) |
| C64 | 0.3784 (3) | 0.4604 (2) | 0.8093 (4) | 0.0576 (9) |
| C65 | 0.3408 (3) | 0.4803 (2) | 0.6828 (3) | 0.0514 (8) |
| C66 | 0.3902 (3) | 0.4393 (2) | 0.5992 (3) | 0.0396 (6) |

Table 2. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|-----------|-------------|------------|-------------|
| Ga1—C1 | 1.961 (3) | Ga2—O2 | 1.998 (2) |
| Ga1—C3 | 1.969 (3) | O1—C11 | 1.376 (3) |
| Ga1—O1 | 1.998 (2) | O2—C41 | 1.371 (3) |
| Ga1—O2 | 2.034 (2) | C1—C2 | 1.516 (4) |
| Ga2—C5 | 1.968 (3) | C3—C4 | 1.460 (5) |
| Ga2—C7 | 1.971 (3) | C5—C6 | 1.524 (4) |
| Ga2—O1 | 1.992 (2) | C7—C8 | 1.518 (5) |
| C1—Ga1—C3 | 119.26 (13) | C5—Ga2—O2 | 100.38 (10) |
| C1—Ga1—O1 | 129.34 (10) | C7—Ga2—O2 | 123.93 (11) |
| C3—Ga1—O1 | 98.83 (11) | O1—Ga2—O2 | 75.99 (7) |
| C1—Ga1—O2 | 98.59 (10) | C11—O1—Ga2 | 127.8 (2) |
| C3—Ga1—O2 | 131.79 (11) | C11—O1—Ga1 | 126.9 (2) |
| O1—Ga1—O2 | 75.04 (7) | Ga2—O1—Ga1 | 105.27 (8) |
| C5—Ga2—C7 | 122.89 (14) | C41—O2—Ga2 | 123.97 (14) |
| C5—Ga2—O1 | 124.19 (10) | C41—O2—Ga1 | 131.91 (14) |
| C7—Ga2—O1 | 101.89 (12) | Ga2—O2—Ga1 | 103.69 (8) |

The methylene H atoms and those on two rings (C1j, C4j; $j = 3\text{--}5$) were located in electron density maps and refined. All other H atoms were placed in calculated positions. All H atoms were given a common refined isotropic atomic displacement parameter.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

The authors would like to thank the EPSRC for support (DJB) and for funds to purchase the X-ray diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1027). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

| | x | y | z | U_{eq} |
|-----|--------------|--------------|-------------|-----------------|
| Ga1 | 0.21043 (2) | 0.27741 (2) | 0.19955 (3) | 0.02715 (9) |
| Ga2 | 0.27804 (2) | 0.20192 (2) | 0.46798 (3) | 0.02833 (9) |
| O1 | 0.1379 (2) | 0.20880 (11) | 0.2896 (2) | 0.0300 (4) |
| O2 | 0.35507 (15) | 0.26867 (10) | 0.3801 (2) | 0.0257 (3) |
| C1 | 0.2226 (3) | 0.4038 (2) | 0.2058 (3) | 0.0366 (6) |
| C2 | 0.3263 (3) | 0.4260 (2) | 0.1689 (4) | 0.0538 (8) |
| C3 | 0.1492 (3) | 0.2010 (2) | 0.0260 (3) | 0.0421 (7) |
| C4 | 0.0988 (6) | 0.2458 (4) | -0.0902 (4) | 0.127 (2) |
| C5 | 0.3894 (3) | 0.1047 (2) | 0.5081 (3) | 0.0374 (6) |
| C6 | 0.4158 (4) | 0.0773 (2) | 0.6420 (3) | 0.0621 (10) |
| C7 | 0.2087 (3) | 0.2564 (2) | 0.5893 (3) | 0.0442 (7) |
| C8 | 0.0885 (4) | 0.2116 (3) | 0.5728 (4) | 0.0719 (11) |
| C11 | 0.0155 (2) | 0.1772 (2) | 0.2404 (3) | 0.0303 (5) |
| C12 | -0.0824 (2) | 0.2343 (2) | 0.1981 (3) | 0.0332 (6) |
| C13 | -0.2054 (3) | 0.2014 (2) | 0.1542 (3) | 0.0418 (7) |
| C14 | -0.2322 (3) | 0.1157 (2) | 0.1549 (4) | 0.0505 (8) |
| C15 | -0.1364 (3) | 0.0596 (2) | 0.1934 (3) | 0.0457 (7) |
| C16 | -0.0118 (2) | 0.0885 (2) | 0.2341 (3) | 0.0351 (6) |
| C21 | -0.0633 (2) | 0.3293 (2) | 0.2020 (3) | 0.0397 (6) |

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A Second Triclinic Polymorph of Bis[1,2-bis(*n*-butylthio)ethylene-1,2-dithiolato-*S,S'*]-nickel

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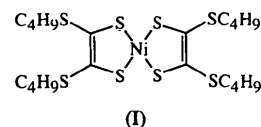
Abstract

The title compound, $[\text{Ni}(\text{C}_{10}\text{H}_{18}\text{S}_4)_2]$, contains discrete centrosymmetric molecules and is a polymorph of a previously reported structure [Charlton, Hill, Underhill, Malik, Hursthouse, Karaulov & Møller (1994). *J. Mater. Chem.* **4**, 1861–1866]. Unlike this earlier form, the title molecule, including the alkyl chains, is essentially planar and contains no short $\text{S}\cdots\text{S}$ intermolecular contacts.

Comment

The title compound, (I), was prepared during the attempted preparation of a nickel complex from a bis(tetrathiafulvalene)thiolate (Le Narvor, Robertson, Wallace, Kilburn, Underhill, Bartlett & Webster, 1996).

The reaction product was not the target species and an inspection of the Cambridge Structural Database (Allen *et al.*, 1991) revealed a compound with the same molecular formula (CCDB refcode: YISDUZ) (Charlton, Hill, Underhill, Malik, Hursthouse, Karaulov & Møller, 1994), which was described as a green solid. The two unit cells were not related and we have here an example of polymorphism.



The crystal structure of (I) is found to contain discrete centrosymmetric molecules (Fig. 1). The atom-labelling scheme has been chosen to match that of Charlton *et al.* (1994) and selected bond distances and angles are listed in Table 2. Not surprisingly, the bond lengths and angles of the two studies agree well and the major differences are in the way that the molecules pack together and in the conformation of one of the chains. The green form (Charlton *et al.*, 1994) has one C_4 chain coplanar with the $\text{Ni}(\text{S}_2\text{C}_2\text{S}_2)$ mean plane and one twisted out of the plane (maximum deviation 4.02 Å), whereas in the brown form (present work), both C_4 residues are essentially coplanar, with a maximum deviation of 0.223 (6) Å from the plane defined by the Ni1, S1, S2, S3, S4, C1 and C6 atoms. There are no short $\text{S}\cdots\text{S}$ intermolecular distances, the shortest being $\text{S2}\cdots\text{S3}(x, y, 1+z)$ of 3.885 (1) Å. The effect of crystal packing on molecular geometry has been discussed recently (Martín & Orpen, 1996) and in the present example, the major differences are in the torsion angles.

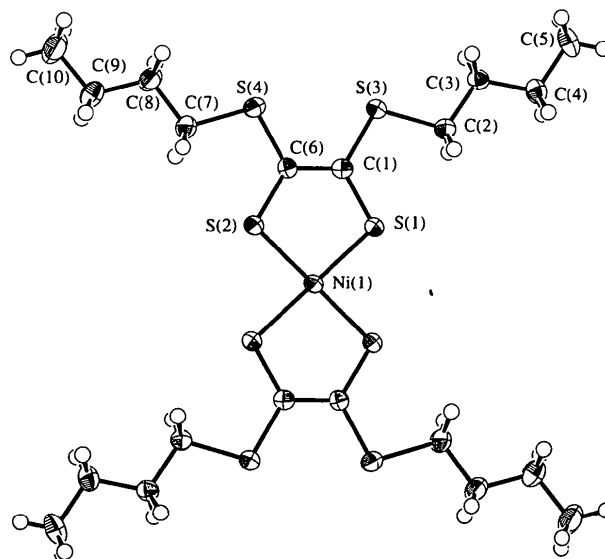


Fig. 1. The molecular structure of $[\text{Ni}(\text{C}_{10}\text{H}_{18}\text{S}_4)_2]$ showing the atom-labelling scheme and displacement ellipsoids drawn at the 60% probability level.