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The germanium(II) ate complex $[Ph_3P^iPr][Ge(OCOMe)_3]$: the first structurally characterized compound containing a discrete $[E^{14(II)}O_3]^{(-)}$ ($E^{14(II)}$ = Si, Ge, Sn or Pb) anion

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An X-ray diffraction study reveals an unusual structure of the new thermally stable germanium(II) ate complex $[Ph_3P^iPr][Ge(OAc)_3]$ (4) containing a discrete $[Ge(OAc)_3]^{(-)}$ anion containing monodentate acetate ligands with a trigonal pyramidal germanium centre. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: germanium(II); acetate; ate complex; crystal structure

INTRODUCTION

There has been much recent interest in divalent derivatives of germanium with oxygen-, nitrogen- and sulfur-donor ligands that effect thermodynamic stabilization through n- or π-donation of electron density to the electron-deficient germanium(II) centre. Although complexes with oxygen-donor ligands have largely been limited to alkoxides and aryloxides,[1] we recently reported the synthesis of first germanium(II) carboxylates—homoleptic $Ge(O_2CMe)_2$ (**1**)[2] and $Ge(O_2CEt)_2$ (**2**; Khrustalev *et al.*, *Appl. Organomet. Chem.*, accepted.) and heteroleptic $(MeCO_2)Ge(OCH_2CH_2NMe_2)$ (**3**).[2] Whereas compounds **2** and **3** were investigated by X-ray crystallography, the structure of **1** could not be determined due to the lack of a crystal suitable for X-ray structure analysis. Therefore, we have focused our attention on the reactivity of **1** with respect to different electrophilic and nucleophilic reagents. It should also be noted that the synthesis of monomeric compound **3**[2] strongly implies the monomeric structure of **1**, in contrast to **2** (which is tetramer). Unexpectedly, we have prepared the new germanium ate complex $[Ph_3P^iPr][Ge(OAc)_3]$ (**4**). Until now only tin(II) tricarboxylate anions in the compounds $K[Sn(O_2CH)_3]$ (**5**),[3] $K[Sn(O_2CCH_2Cl)_3]$ (**6**),[4] $Ca[Sn(O_2CCH_3)_3]_2$ (**7**)[5] and $Sr[Sn(O_2CCH_2Cl)_3]_2$ (**8**)[6] were known. The ate complex **4** is the first example of the compound containing the germanium(II) tricarboxylate anion. The synthesis of **4** will be described elsewhere. In this communication we report about the X-ray diffraction study of its crystal structure.

EXPERIMENTAL

Ate complex **4** is isolated as a white, thermally stable crystalline material that is soluble in hot pyridine and moderately soluble in tetrahydrofuran at room temperature, and which is very sensitive to the traces of oxygen and moisture. Compound **4** gave satisfactory microanalytical and ^1H and ^{13}C NMR spectroscopic data consistent with its molecular structure, which was definitively established by a single-crystal X-ray diffraction study. NMR spectra

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were recorded on Bruker AM-360 NMR spectrometer at 360.134 MHz (^{1}H) and 90.555 MHz (^{13}C). Chemical shifts are relative to SiMe$_4$. The accuracy of the coupling constant determination is ±0.1 Hz, and the accuracy of the chemical shift measurements is ±0.01 ppm for ^{1}H and ±0.05 ppm for ^{13}C.

[Ph$_3$P^{i}Pr]$^{(+)}$[Ge(OCOMe)$_3$]$^{(-)}$ (4)

M. p. = 150 °C (sealed capillary). Anal. Found: C, 58.58; H, 5.53. Calc. for $C_{27}H_{31}GeO_6P$: C, 58.42; H, 5.61%. ^{1}H NMR (C_5D_5N, 298 K): δ 1.14 (dd, 6H, Me$_2$CP, $^3J_{PH} = 18.8$ Hz, $^3J_{HH} = 6.8$ Hz), 2.06 (s, 9H, Me), 4.28 (d/sept, 1H, PCH, $^3J_{PH} = 11.1$ Hz, $^3J = 6.8$ Hz), 7.66–8.14 (m, 15H, ArP). ^{13}C NMR (C_5D_5N, 298 K): δ 16.39 (Me$_2$CP, $^3J_{PH} = 2.0$ Hz), 21.69 (CP, $^3J_{PH} = 47.0$ Hz), 23.95 (Me), 118.5 (C_i, $^1J_{PC} = 83.1$ Hz), 134.5 (C_o, $^2J_{PC} = 9.2$ Hz), 130.7 (C_m, $^3J_{PC} = 12.1$ Hz), 134.9 (C_p, $^4J_{PC} = 3.0$ Hz).

X-ray structure determination of 4

Data were collected on a Bruker three-circle diffractometer equipped with a SMART 1000 CCD detector ($T = 110$ K, Mo Kα radiation, ϕ and ω scan mode, $\theta_{max} = 30°$) and corrected for Lorentz and polarization effects and for absorption.[7] $C_{27}H_{31}GeO_6P$, $M = 555.08$, monoclinic, space group $P2_1/c$, $a = 9.6120(4)$, $b = 12.2852(5)$, $c = 22.1274(8)$ Å, $\beta = 95.656(1)°$, $V = 2600.2(2)$ Å^3, $Z = 4$, μ(Mo Kα) = 1.279 mm^{-1}, 24 265 reflections measured. Refinement on all F^2, final $R_1 = 0.030$ (5583 data with $I > 2\sigma(I)$), $wR_2 = 0.066$ (all 7525 data). The structure was solved by direct methods and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were located in difference Fourier syntheses and refined isotropically. All calculations were carried out by use of the SHELXTL PLUS (PC Version 5.10) program.[8] CCDC deposition number: 206723.

RESULTS AND DISCUSSION

Crystals of **4** suitable for X-ray crystallography were obtained from pyridine solution. The molecular structure of the anion of **4**, along with the atomic numbering scheme and selected bond lengths and angles, is shown in Fig. 1. Compound **4** crystallizes as discrete cations and anions; the shortest cation···anion P···Ge distance is 5.578(1) Å and the shortest Ge···Ge distance is 7.500(1) Å. The shortest interionic C–H···O contacts in the structure of **4** are: O(1)···H(23)–C(23) $(1 + x, 1 + y, z)$ (O···C 3.386(2), O···H 2.58(2) Å, O···H–C 147(1)°); O(2)···H(26c)–C(26) $(-x, 0.5 + y, 0.5 - z)$ (O···C 3.460(2), O···H 2.65(2) Å, O···H–C 143(1)°); O(3)···H(21)–C(21) $(-x, 1 - y, 1 - z)$ (O···C 3.285(2), O···H 2.43(2) Å, O···H–C 151(1)°); O(4)···H(14)–C(14) $(-x, 0.5 + y, 0.5 - z)$ (O···C 3.061(2), O···H 2.27(2) Å, O···H–C 138(1)°); O(6)···H(16)–C(16) (O···C 3.266(2), O···H 2.55(2) Å, O···H–C 137(1)°). Rowland and Taylor[9] have shown that most oxygen-containing organic compounds in crystals contain intermolecular C–H···O contacts with the C···O separation ~3.24 Å (av.), which must be regarded as a normal (non-bonded) van der Waals C···O distance. Moreover, Desiraju[10] has found that, in crystals, mainly, C–H···O contacts having parameters $2.00 < d(\text{O}\cdots\text{H}) < 2.30$ Å and $150 < \theta(\text{O}\cdots\text{H–C}) < 180°$ are significant. As can be seen, ate complex **4** does not have such significant interactions.

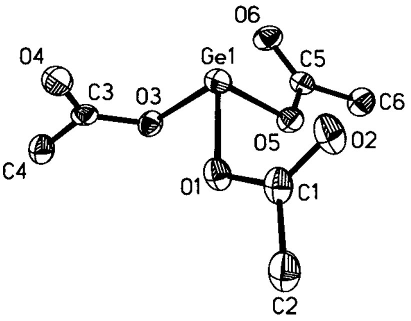

Figure 1. Structure of the anion of **4** with 50% probability ellipsoids and with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–O(1) 1.936(1), Ge(1)–O(3) 1.948(1), Ge(1)–O(5) 1.921(1), O(1)–Ge(1)–O(3) 87.72(4), O(1)–Ge(1)–O(5) 88.30(5), O(3)–Ge(1)–O(5) 89.36(4).

Interestingly, regardless of the absence of additional stabilizing cation–anion interactions, ate complex **4** is characterized by high thermal stability.

The germanium atom in the anion adopts a distorted trigonal pyramidal geometry with a stereochemically active lone pair, as is commonly observed for compounds of the form [E$^{14(\text{II})}$X$_3$] (E^{14} = Ge, Sn, Pb).[11] Each of the three GeOCOMe units is almost perfectly planar and oriented in a 'propeller-like' fashion with respect to each other. The [Ge(OAc)$_3$]$^{(-)}$ anion has overall idealized C_3 symmetry, although the Ge–O distances (1.921(1), 1.936(1) and 1.948(1) Å) differ significantly from each other, and the O–Ge–O angles are 87.72(4), 88.30(5) and 89.36(4)°. Surprisingly, previously reported Group 14 ate complexes with thiolate or selenolate ligands, which contain discrete [E^{14}X$_3$]$^{(-)}$ anions (E^{14} = Ge, Sn, Pb; X = SPh, SePh), also exhibit the same remarkable structural features.[12–14] Although it is possible to attribute the variation in O–Ge–O bond angles to crystal packing forces, there seems no obvious explanation for the disparity in the chemically equivalent Ge–O bond lengths. It is important to point out that these peculiarities are evidently absent in the structures of **5**–**8**, which are aggregated via the alkaline metal–oxygen or alkaline-earth metal–oxygen coordination interactions (for instance, the analogous tin(II) [Sn(O$_2$CMe)$_3$]$^{(-)}$ anion in complex **7** has a crystallographically imposed the threefold axis, but, consequently, cannot have the disparity neither in the O–Sn–O bond angles nor in the Sn–O bond lengths), although it is difficult to discuss their geometric features in detail owing to the low accuracy of the X-ray diffraction experiments have been carried out.

The Ge–O bond lengths in **4** are comparable to that in (AcO)Ge(OCH$_2$CH$_2$NMe$_2$) [1.938(1) Å],[2] but they considerably exceed the Ge(II)–O bond lengths in the alkoxide $[(^tBu)_3CO]_2Ge$[15] (1.896(16) and 1.832(11) Å) and in the aryloxide $[(2,6\text{-}(^tBu)_2\text{-}4\text{-}Me(C_6H_2)O]_2Ge$[16] (1.802(8) and 1.812(7) Å). It should also be pointed out that they lie within the range of terminal (1.899(2) Å) and bridging (1.977(2) and 2.021(2) Å) bond lengths in tetramer **2** (Khrustalev *et al.*, *Appl. Organomet. Chem.*, accepted.).

The acetate ligands in **4** are monodentate and exhibit no intra-chelate Ge–O interactions. Despite the fact that the Ge···O distances [Ge···O(2) 2.869(2), Ge···O(4) 2.949(2) and Ge···O(6) 2.865(2) Å] in **4** are slightly smaller than the sum of the van der Waals radii for the germanium and oxygen atoms (~3.3 Å[17,18]), they cannot be considered the binding contacts. The lengths of these distances are restrained by the O–C–O angles (O(1)–C(1)–O(2) 123.23(16), O(3)–C(3)–O(4) 123.89(15) and O(5)–C(5)–O(6) 122.94(14)°) craving for 120° in accordance with sp^2 hybridization. The structure of the $[Ph_3P^iPr]^{(+)}$ cation is unexceptional.

The synthesis and structures of a series of other germanium(II) acyloxy derivatives will be reported by us elsewhere.

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