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New Germanium Complexes Containing Ligands Based on 4,6-Di-*tert*-butyl-N-(2,6-diisopropylphenyl)-o-iminobenzoquinone in Different Redox States

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The exchange reaction of lithium *o*-amidophenolate, (AP)Li₂, derived from the reaction of 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone (imQ) with GeCl₄ in hexane or thf leads to (AP)₂Ge (**1**) (AP is a dianion of imQ). The latter was also obtained by the interaction of GeCl₂-dioxane and (ISQ)Li in toluene (ISQ is a radical anion of imQ). The reaction of (AP)Li₂ with GeCl₂-dioxane in thf results in the formation of germylene **2**, [(AP)Ge (**2**)], which reduces neutral imQ to give compound **1**. The exposure of **1** in thf to anhydrous HCl in a 1:1 molar ratio leads to its *o*-aminophen-

Introduction

Diamide ligands were shown to be very useful in obtaining stable derivatives of group 14 elements,^[1,2] particularly germanium,^[1g-1k] in the divalent state. A significant part of these compounds is based on diazabutadiene-type ligands. One of their most important features is the ability to form not only dianion derivatives but radical anion complexes containing divalent germanium.^[1h-1g] Redox-active ligands like diazabutadienes, which can be involved in redox reactions without losing their coordination ability, are of special interest. The introduction of such ligands into the metal coordination sphere will expand its reactivity. Moreover, EPR spectroscopy gives essential information about the structure and behaviour of this type of compounds. However, diazabutadiene derivatives are quite rare in Ge^{IV} chemistry. To date, only a few tetravalent germanium diamides on the basis of substituted diazabutadienes have been described.^[2a-2d] All of these compounds include nonchelating groups besides the diamide ligand. The existence of more than one diazabutadiene ligand in a germanium(IV) environment was shown to be impossible.^[1c] Nevertheless, the use of benzannulated diamides yields the GeN_4 core.^[2e-2f] In accordance with the preceding discussion, the chemistry of complexes based on the benzannulated 4,6-ditert-butyl-N-(2,6-diisopropylphenyl)-o-iminoquinone ligand

 [a] G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences Tropinina Str. 49, 603950, Nizhny Novgorod, GSP-445, Russia Fax: +7-8314-627497 E-mail: pial@iomc.ras.ru olato derivative, (AP)(APH)GeCl (3). Free imQ inserts into the Ge–H bond of $(C_6F_5)_3$ GeH in thf to give $(C_6F_5)_3$ Ge(APH) (4). It is another way of obtaining complexes with protonated ligands such as APH. Compound 3 can be easily oxidized by air to form the stable paramagnetic complex (AP)(ISQ)GeCl (5). Complexes 1 and 3–5 were structurally investigated by using single-crystal X-ray diffraction.

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(imQ) (Scheme 1) is of interest. In comparison with diazabutadienes, the substitution of one imino fragment by a carbonyl function appreciably changes both the steric situation in the coordination sphere of the metal and the redox properties of the active ligand.



Scheme 1.

Recently we have reported the synthesis of tin complexes with *o*-amidophenolato ligands on the basis of imQ containing one or two *o*-iminoquinone substituents and the metal in different valence states,^[3] (Scheme 2) in contrast to the corresponding diamido complexes.^[1b,1c,1e] Afterwards, the stable radical tin derivative based on this ligand has been obtained and structurally characterized.^[4]

It is noteworthy that the whole potential versatility of *o*iminoquinone complexes, such as ability of the ligand to exist in the protonated state, was not manifested for tin derivatives. In the present paper we show the versatile behaviour of imQ as the ligand that is able to exist in different redox and valent states by the example of germanium complexes.





Results and Discussion

To obtain germanium complexes with imQ-based ligands, we used exchange reactions of germanium chlorides with alkali metal *o*-iminoquinone salts. Earlier this was shown to be a suitable method to synthesize tin complexes of the same type.^[3,4] Lithium *o*-amidophenolate, (AP)Li₂,^[4] reacts with tetrachlorogermane in hexane or thf solution to yield the corresponding bis(*o*-amidophenolato) compound (AP)₂Ge (1) (Scheme 3). Complex 1 was isolated from hexane as colourless crystals suitable for X-ray analysis.



Ar = 2,6-diisopropylphenyl

Scheme 3.

It is noteworthy that, even when the reaction was carried out in the strongly coordinating thf solvent, the coordination number of the Ge^{IV} atom was four, in contrast to that in the similar bis(*o*-amidophenolato)tin(IV) derivative (AP)₂Sn(thf)^[3] and in the bis(catecholato)germanium(IV) complex,^[5a] which contain pentacoordinate metal centres due to a thf molecule bonded as a donor-acceptor.

As we have found previously, the exchange reaction of $(AP)Li_2$ with Ph_2SnCl_2 in hexane is accompanied by a redox side-reaction between tin(IV) and the *o*-amidophenolato ligand to give *o*-iminosemiquinonate derivatives.^[4] In comparison with tin(IV), germanium(IV) is a relatively weaker oxidant, and as a result, the redox reaction does not take place during the formation of complex **1**.

Complex 1 can be obtained in another way by using $GeCl_2$ ·dioxane and the lithium derivative, (ISQ)Li, of ISQ, which is a radical anion of imQ, as the starting reagents (Scheme 3). Lithium *o*-iminosemiquinolate was prepared by the reaction of (AP)Li₂ with an equimolar quantity of free imQ in toluene. While the reactants were mixed, the darkblue colour of the lithium radical anion salt disappeared and the reaction mixture turned colourless, indicating the formation of a diamagnetic compound. The product was isolated and identified as complex 1. We were unable to obtain any evidence for the primary formation of derivative $Ge(ISQ)_2$ in this reaction; but if this is true, the triplet germylene species should engage in a double radical recombination reaction leading to complex 1.

The reaction of GeCl_2 ·dioxane with (AP)Li₂ in thf yields the corresponding *o*-amidophenolate derivative on the basis of the low-valent germanium(II) species, (AP)Ge (2) (Scheme 4), as a red volatile viscous resin. Complex 2 did not form crystals, neither from solution nor during sublimation. Even when stored for several months in a sealed tube, it stayed amorphous.



Scheme 4.

Germylene 2 initially adds *o*-iminoquinone in toluene or thf to give complex 1 (Scheme 5). The product of imQ addition to (AP)Ge (2) was identified by melting point and ¹H NMR analysis data.



Ar = 2,6-diisopropylphenyl

Scheme 5.

The exposure of **1** in thf to anhydrous HCl in a 1:1 molar ratio results in N–Ge bond cleavage and hydrogen chloride addition leading to (*o*-aminophenolato)germanium(IV) derivative (AP)(APH)GeCl (**3**) (Scheme 6). Features of NH-derivative (AP)(APH)GeCl are demonstrated by ¹H NMR and IR spectra.

Another way to synthesize *o*-aminophenolato germanium derivatives is the insertion of *o*-iminoquinone into the Ge–H bond of germanes. $(C_6F_5)_3$ GeH reacts with imQ in thf to give the corresponding *o*-aminophenolate, $(C_6F_5)_3$ -Ge(APH) (4) (Scheme 7).

The considerable difference in the germanium coordination environment between complexes **3** and **4** results in the significant discrepancy in Ge–N bonding. The amine hydrogen signal in the ¹H NMR spectrum appears at a chemi-



Ar = 2,6-diisopropylphenyl

Scheme 6.



Ar = 2,6-diisopropylphenyl

Scheme 7.

cal shift value of 7.08 ppm for **3** and 5.63 ppm for **4**. Moreover, the v_{N-H} absorption band in the IR spectra for **3** and **4** are 3262 and 3386 cm⁻¹, respectively. NMR and IR spectroscopy data for **3** are typical for the coordinated amine group,^[6] while in **4** the NH-fragment stays uncoordinated. This fact was confirmed by the structural investigations.

The *o*-aminophenolato ligand in **3** can easily be oxidized by oxygen to the *o*-iminosemiquinonato substituent. The process takes place in acetone under ambient conditions, yielding the dark-green radical anion complex (AP)(ISQ)-GeCl (**5**) (Scheme 8).

Complex 5 is air-stable both in the solid state and in solution for several hours. It has a well-resolved X-band EPR spectrum with $g_i = 2.0022$ in toluene at ambient temperature (Figure 1). The hyperfine structure arises from hyperfine coupling (HFC) of an unpaired electron with magnetic nuclei ¹H (99.98%, I = 1/2, $\mu_{\rm N} = 2.7928$), ¹⁴N $(99.63\%, I = 1, \mu_N = 0.4037), {}^{35}Cl (75.77\%, I = 3/2, \mu_N =$ 0.8218) and ³⁷Cl (24.23%, I = 3/2, $\mu_{\rm N} = 0.6841$).^[7] The splitting parameters are: $A_i(2^1H) = 2.1 \text{ G}, A_i(2^{14}N) = 2.9 \text{ G},$ $A_{i}({}^{35}\text{Cl}) = 1.3 \text{ G}, A_{i}({}^{37}\text{Cl}) = 1.1 \text{ G}.$ The observation of HFC with two nitrogen and two hydrogen atoms indicates radical centre delocalization over two ligands. This interligand electron exchange is also confirmed by ¹⁴N- and ¹H-HFC constants, which are nearly twice lower than those for the (ISQ)SnPh₂Cl complex.^[4] The character of the EPR spectrum for (AP)(ISQ)GeCl stays unchanged in the temperature interval 220-300 K.



tBu

Ar

/Ru

Ar

Cl

3

tBu

Figure 1. Experimental X-band EPR spectrum of 5 in toluene at 290 K (a) and its simulation (b).

It is necessary to note that complex 5 is a rare example of a stable germanium derivative that contains a paramagnetic ligand. Until now, only a few examples were known. The stable paramagnetic germylene based on the 1,2-bis(arylimino)acenaphthene radical anion has been obtained by Fedushkin and co-workers.^[1h] Stable mono- and diradical germanium(IV) complexes reported in papers^[5b,5c] contain the tridentate 3,5-di-tert-butyl-1,2-quinone-1-(2-hydroxy-3,5-di-tert-butylphenyl)imine anion. There are some reports about the formation of stable germanium derivatives with the radical anion of 3,6-di-tert-butyl-o-benzoquinone; however, these compounds were not isolated as solids but were only established in solutions by EPR spectroscopy.^[5d,5e] Moreover, different radical derivatives from the reaction of elemental germanium with 3,5-di-tert-butyl-obenzoquinone were postulated in ref.,[5f] but structures assigned for some of them are not incontrovertible.



Scheme 8.

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Molecular Structures of 1, 3, 4 and 5

Molecular structures of 1, 3, 5 and 4 are shown in Figures 2, 3, 4 and 5, respectively. Selected bond lengths and angles are given in Table 1. The crystal data collection and structure refinement data are listed in Table 2. Crystals suitable for X-ray analysis were obtained from hexane for 1 and 3, a 2:1 mixture of hexane/dichloromethane for 4 and acetone for 5.



Figure 2. PLATON^[20] presentation of molecule 1. (A) H atoms and methyl groups of isopropyl substituents are omitted for clarity. (B) H atoms and *tert*-butyl substituents are omitted for clarity.



Figure 3. PLATON^[20] presentation of molecule **3**. H atoms are omitted for clarity.



Figure 4. PLATON^[20] presentation of molecule 5. H atoms are omitted for clarity.



Figure 5. PLATON^[20] presentation of molecule 4. H atoms and methyl groups of isopropyl and *tert*-butyl substituents are omitted for clarity.

The central germanium atom in 1 (Figure 2) is coordinated to two nitrogen and two oxygen atoms of *o*-amidophenolato ligands in a distorted tetrahedral geometry. The dihedral angle between the two chelate rings is $85.74(4)^\circ$. The angle O(1)–Ge(1)–O(2) [108.36(4)°] is notably less than the angle N(1)–Ge(1)–N(2) [126.96(5)°] because of the steric repulsion of *N*-aryl groups.

The distances Ge–O [1.786(1) and 1.785(1) Å] and Ge– N [1.798(1) and 1.800(1) Å] are nearly equal. They are noticeably shorter than sums of covalent radii of germanium and oxygen and of germanium and nitrogen (1.88 and 1.93 Å respectively),^[7] and are similar to those observed for Ge^{IV} complexes simultaneously containing *O*- and *N*bonded ligands (1.789–1.828 and 1.742–1.820 Å correspondingly).^[2c,8]



Table 1. Selected bond lengths [Å] and angles [°] for complexes 1 and 3-5.

Bond lengths	1	3	4	5	
C				1 st mol (A)	2 nd mol (B)
Ge(1)-O(1)	1.786(1)	1.807(1)	1.785(3)	1.874(1)	1.880(1)
Ge(1) - O(2)	1.785(1)	1.816(1)	_	1.870(1)	1.880(1)
Ge(1) - N(1)	1.800(1)	1.840(2)	3.261(5)	1.884(1)	1.879(1)
Ge(1) = N(2)	1 798(1)	2 136(2)	_	1 887(1)	1 879(1)
O(1) - C(1)	1.384(2)	1.385(2)	1 395(5)	1 339(2)	1 335(2)
O(1) - O(1) O(2) - O(27)	1.387(2)	1.363(2)	1.555(5)	1.339(2) 1 340(2)	1.335(2)
N(1) C(2)	1.337(2) 1.421(2)	1.303(2) 1 400(2)	- 1 420(5)	1.340(2) 1.368(2)	1.333(2) 1.377(2)
N(1) = C(2) N(1) = C(15)	1.421(2) 1.424(2)	1.409(2) 1.432(2)	1.420(3) 1.448(5)	1.300(2) 1.449(2)	1.377(2) 1.442(2)
N(1) = C(13) N(2) = C(28)	1.434(2)	1.452(2) 1.465(2)	1.440(5)	1.440(2) 1.277(2)	1.442(2) 1.277(2)
$N(2) = C(2\delta)$	1.419(2)	1.403(2)	—	1.577(2)	1.377(2)
N(2) - C(41)	1.438(2)	1.4/3(2)	-	1.440(2)	1.442(2)
C(1) - C(6)	1.390(2)	1.394(3)	1.396(5)	1.406(3)	1.396(2)
C(1)-C(2)	1.405(2)	1.395(2)	1.407(6)	1.419(3)	1.437(2)
C(2) - C(3)	1.383(2)	1.387(3)	1.390(6)	1.402(2)	1.391(2)
C(3) - C(4)	1.400(2)	1.401(3)	1.389(6)	1.377(3)	1.382(2)
C(4) - C(5)	1.389(2)	1.382(3)	1.395(6)	1.415(3)	1.415(3)
C(5) - C(6)	1.404(2)	1.403(3)	1.396(6)	1.393(2)	1.392(2)
C(27)–C(32)	1.396(2)	1.415(3)	-	1.404(3)	1.396(2)
C(27)–C(28)	1.400(2)	1.384(3)	_	1.418(2)	1.437(2)
C(28)–C(29)	1.381(2)	1.384(3)	_	1.398(2)	1.391(2)
C(29) - C(30)	1.391(2)	1.376(3)	_	1.390(3)	1.382(2)
C(30) - C(31)	1.395(2)	1.400(3)	_	1.407(3)	1.415(3)
C(31) - C(32)	1.399(2)	1.387(3)	_	1.388(2)	1.392(2)
Ge(1)-Cl(1)	_	2.182(1)	_	2.174(1)	2.158(1)
Ge(1) - C(27)	_	_	1 950(4)	_	_
Ge(1) = C(33)	_	_	1 935(4)	_	_
Ge(1)-C(39)	_	_	1.954(4)	_	_
Angles			· · · · · · · · · · · · · · · · · · ·	·	
$\frac{1}{O(2)}$ C ₂ (1) O(1)	109.26(4)	149.07(6)		171 40(4)	172 20(7)
O(2) - O(1) - O(1) O(2) - O(1) - O(1)	108.30(4)	146.92(0)	—	1/1.49(4)	1/2.30(7)
O(2)-Ge(1)-N(2)	92.36(5)	83.48(0)	_	85.28(5)	85.52(5)
O(1)-Ge(1)-N(2)	118.51(5)	82.26(6)	-	90.87(5)	91.27(5)
O(2)-Ge(1)-N(1)	118.89(4)	95.79(6)	-	91.32(6)	91.27(5)
O(1)-Ge(1)-N(1)	92.31(5)	88.79(6)	57.59(6)	85.39(6)	85.51(5)
N(2)-Ge(1)-N(1)	126.96(5)	160.53(7)	_	130.42(5)	130.67(8)
C(1)-O(1)-Ge(1)	109.25(8)	111.29(11)	120.5(2)	112.71(11)	112.91(10)
C(27)-O(2)-Ge(1)	108.71(7)	117.05(11)	_	112.72(11)	112.91(10)
C(2)-N(1)-C(15)	120.71(11)	121.60(15)	112.9(3)	120.29(13)	121.25(11)
C(2)-N(1)-Ge(1)	108.06(9)	110.13(12)	80.64(6)	112.43(11)	112.54(10)
C(15)-N(1)-Ge(1)	130.41(9)	127.95(12)	165.44(9)	127.28(11)	125.98(10)
C(28)-N(2)-C(41)	119.95(11)	114.29(14)	_	119.43(12)	121.25(11)
C(28)-N(2)-Ge(1)	107.63(8)	105.46(10)	_	111.87(11)	112.54(10)
C(41)-N(2)-Ge(1)	131.87(9)	125.36(11)	_	128.32(11)	125.98(10)
O(1) - Ge(1) - Cl(1)	_	105.26(4)	_	94.38(3)	93.85(3)
O(2)-Ge(1)-Cl(1)	_	102.00(4)	_	94.13(3)	93.85(3)
N(1)-Ge(1)-Cl(1)	_	109.85(5)	_	114.14(3)	114.67(4)
N(2)-Ge(1)-Cl(1)	_	89.24(4)	_	115.44(4)	114.67(4)
O(1)-Ge(1)-C(33)	_	_	108.73(14)	_	_
O(1)-Ge(1)-C(27)	_	_	106.30(14)	_	_
C(33)-Ge(1)-C(27)	_	_	115.36(16)	_	_
O(1) - Ge(1) - C(39)	_	_	108 71(15)	_	_
$C(33)_Ge(1)_C(30)$	_	_	111 67(15)	_	_
C(27)-Ge(1)-C(39)	_	_	105.77(17)	_	_
			× /		

C–O bond lengths [1.384(2) and 1.387(2) Å] are typical for analogous (*o*-amidophenolato)tin complexes (1.351–1.400 Å),^[3,4] and C–N distances [1.421(2) and 1.419(2) Å] are slightly longer than those in similar Sn derivatives (1.398–1.408 Å).^[3,4] At the same time, C–O and C–N bond lengths are significantly longer than those in the *o*-iminosemiquinonate tin(IV) complex [1.298(4) and 1.334(4) Å respectively].^[4]

Hence, also taking into account that a toluene solution of compound 1 is EPR-silent and has a rather well-resolved

¹H NMR spectrum, the compound can be described as a complex containing a Ge^{IV} core bonded with two *o*-amido-phenolato ligands.

As can be seen from its molecular structure (Figure 2B), complex 1 contains two nonequivalent pairs of isopropyl substituents. The ¹H NMR spectrum of 1 in $[D_8]$ toluene contains two signals attributed to CH groups and four signals to the *i*Pr CH₃ groups, indicating that the above-mentioned nonequivalence caused by steric hindrances to free rotation of Ph(*i*Pr)₂ substituents remains in solution.

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Complex	1	3·hexane	4	5
Empirical formula	C ₅₂ H ₇₄ GeN ₂ O ₂	C ₅₈ H ₈₉ ClGeN ₂ O ₂	C44H38F15GeNO	C ₅₂ H ₇₄ ClGeN ₂ O ₂
Formula weight	831.72	954.35	954.34	867.17
Temperature [K]	100(2)	100(2)	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	PĪ	C2/c
Unit cell dimensions				
a [Å]	12.3194(4)	13.7975(6)	10.4360(14)	40.1711(11)
<i>b</i> [Å]	21.1575(7)	17.6923(7)	10.7926(15)	18.4703(5)
c [Å]	19.383(7)	22.9534(9)	20.423(3)	24.8586(7)
a [°]			104.359(2)	
β [°]	106.3360(10)	98.7990(10)	91.794(2)	126.2130(10)
γ [°]			107.108(2)	
Volume [Å ³]	4849.5(3)	5537.2(4)	2116.2(5)	14881.4(7)
Ζ	4	4	2	12
Density (calculated) [g cm ⁻³]	1.139	1.145	1.498	1.161
Absorption coefficient [mm ⁻¹]	0.670	0.642	0.825	0.710
Crystal size [mm ³]	$0.35 \times 0.15 \times 0.06$	$0.24 \times 0.18 \times 0.14$	$0.63 \times 0.48 \times 0.25$	$0.40 \times 0.37 \times 0.06$
θ range for data collection [°]	1.93-26.00	1.89-25.00	2.03-29.18	2.03-26.00
Reflections collected	41235	30273	21637	63179
Independent reflections	9518 [R(int) = 0.0406]	9721 [$R(int) = 0.0387$]	10956 [R(int) = 0.0281]	14583 [R(int) = 0.0643]
Completeness to $\theta = 25.00$	100.0%	99.6%	95.8%	99.7%
Absorption correction	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
Max, and min, transmission	0.9609 and 0.7992	0.9155 and 0.8612	0.8202 and 0.6243	0.9586 and 0.7643
Refinement method	full-matrix least-	full-matrix least-	full-matrix least-	full-matrix least-
	squares on F^2	squares on F^2	squares on F^2	squares on F^2
Data/restraints/parameters	9518/0/810	9721/41/877	10956/6/593	14583/14/1193
Final <i>R</i> indices	$R_1 = 0.0392.$	$R_1 = 0.0472.$	$R_1 = 0.0879.$	$R_1 = 0.0445.$
$[I > 2\sigma(I)]^{[a,b]}$	wR2 = 0.0978	wR2 = 0.1235	wR2 = 0.2287	wR2 = 0.0983
<i>R</i> indices	$R_1 = 0.0504$	$R_1 = 0.0665.$	$R_1 = 0.0925.$	$R_1 = 0.0780.$
(all data)	wR2 = 0.1024	wR2 = 0.1322	wR2 = 0.2304	wR2 = 0.1084
Goodness-of-fit on $F^{2[c]}$	1.044	1.035	1.158	1.000
Largest diff. peak and hole $[e Å^{-3}]$	0.576 and -0.288	1.253 and -0.506	1.343 and -0.937	0.787 and -0.365

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $\omega R = R(\omega F^2) = \{ \sum [\omega(F_o^2 - F_c^2)^2] / \sum [\omega(F_o^2)^2] \}^{1/2}; \ \omega = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP], \ P = [2F_c^2 + \max(F_o, 0)] / 3.$ [c] $S = Goof = \{ \sum [\omega(F_o^2 - F_c^2)^2] / (n-p) \}^{1/2}, \ where \ n \text{ is the number of reflections, and } p \text{ is the number of refined parameters.} \}$

The pentacoordinated Ge atom in complex 3 has a distorted square-pyramidal environment (Figure 3). The imQ ligands form the base of the pyramid, and the chlorine atom occupies an apical site. Notably, Cl(1) is shifted from the N(1) towards the N(2) atom in the hypothetical plane N(1)Cl(1)Ge(1)N(2) [the sum of bond angles N(1)-Ge(1)-N(2)-Ge(1)-Cl(1)Cl(1), and N(1)-Ge(1)-N(2)is 359.62(16)°]: the angles N(1)-Ge(1)-Cl(1) and N(2)-Ge(1)-Cl(1) are 109.85(5)° and 89.24(4)° respectively. Apparently, this distortion is determined by intramolecular Cl(1)···H(2) interaction. The Cl(1)···H(2) distance is 2.59(3) Å, which is significantly less than the sum of the van der Waals radii (2.97 Å).^[9] The heteroatom-to-germanium-to-heteroatom angles reveal the difference, which is unusual for five-coordinate complexes of the ML₂X type (L is an *o*-iminobenzoquinonato-based ligand): the value of the angle O(1)-Ge(1)-O(2) [148.92(6)°] is less than that for N(1)-Ge(1)-N(2) [160.53(7)°], while in transition-metal complexes $M(ISQ)_2Hal$ (M = Co, Fe, Mn) a decrease in the N-M-N angle relative to O-M-O is usual.^[10f]

The first organic ligand is the dianion *o*-amidophenolate. The distances O(1)-C(1) of 1.385(2) Å and N(1)-C(2) of 1.409(2) Å are close to the distances in the bis(*o*-amidophenolato)germanium complex $(AP)_2Ge$. The carbon ring C(1)C(6) also has aromatic character with an average C–C distance of 1.394 ± 0.015 Å.

The second ligand shows the remarkable features of a protonated *o*-aminophenolato ligand. While the N(1) atom is three-coordinate (sp² hybridized) with a nearly planar geometry, the N(2) atom is protonated and sp³ hybridized. Additionally, the N(2)–C(28) [1.465(2) Å] bond is significantly elongated in comparison with that in compound **1**, and it is typical for those in *o*-aminophenolato transitionmetal complexes (1.46–1.47 Å).^[10a,10b] The distances O(2)–C(27) and O(1)–C(1) [1.363(5) and 1.385(2) Å, respectively] lie in the range that is usual for phenolates (1.35–1.39 Å).^[10a–10d,f,11] All C–C bond lengths of the C(27)C(32) ring, with an average value of 1.391 Å, are similar to those in the C(1)C(6) aromatic ring.

The Ge(1)–O(1) and Ge(1)–O(2) covalent bonds [1.807(1) and 1.816(1) Å respectively] are quite close in length; at the same time the Ge(1)–N(1) bond is considerably shorter than Ge(1)–N(2) [1.840(2) and 2.136(2) Å correspondingly] as a result of the donor-acceptor nature of the Ge(1)–N(2) bond in contrast to the covalent bond Ge(1)–N(1).



The Ge(1)–Cl(1) distance [2.182(1) Å] is nearly identical to the sum of the covalent radii of chlorine and germanium (2.18 Å).^[7]

Thus, complex **3** contains the *o*-amidophenolato dianion and *o*-aminophenolato anion ligands chelating the germanium(IV) chloride moiety.

There are two crystallographically independent molecules of complex (AP)(ISQ)GeCl (5) in the unit cell, one of which is in the common position (A), whereas the other is disposed on the C_2 axis (B). Both molecules can be considered as distorted square pyramids with organic ligands in the base, as in compound 3. The chlorine atom also occupies an apical site (Figure 4).

The bond of Ge to the apical chlorine atom for the second (symmetrical) molecule, Ge(1)–Cl(1) [2.1579(6) Å], is shorter than the same bond in the first (unsymmetrical) molecule, Ge(2)–Cl(2), [2.1741(4) Å].

The bond angles O–Ge–O and N–Ge–N in both molecules are nearly equal: O(1A)–Ge(1A)–O(2A) is 171.49(4)° and O(1B)–Ge(2B)–O(1B') is 172.30(7)°; N(1A)–Ge(1A)– N(2A) is 130.42(5)° and N(3B)–Ge(2B)–N(3B') is 130.67(8)°.

We did not find a significant difference in the geometrical characteristics of the ISQ and AP ligands in 5. Comparison of the geometrical parameters of these ligands in known derivatives^[4,10] with the ones in 5 shows that the C–O and C-N bond lengths in 5 have intermediate values between the analogous distances in ISQ and AP ligands of other known derivatives. The O(1)-C(1) and N(1)-C(2) bond lengths for the first ligand [1.339(2) and 1.368(2) Å respectively] are quite close to the O(2)-C(27) and N(2)-C(28)distances [1.340(2) and 1.377(2) Å respectively] for the second one. They are longer than the corresponding bond lengths in o-iminobenzosemiquinonato complexes (1.29-1.32 and 1.33–1.36 Å)^[4,10] and slightly shorter than those in o-amidophenolates (C-O 1.35-1.36 Å, C-N 1.38-1.39 Å).^[4,10] It should be noted that the six-membered carbon rings C(1)C(6) and C(27)C(32) are quite distorted. The quinoid pattern is observed for both ligands: two shorter bonds are separated by longer bonds (Table 1).

The Ge(1)–O(1) [1.874(1) Å] and Ge(1)–N(1) [1.884(1) Å] distances are close to the Ge(1)–O(2) [1.870(1) Å] and Ge(1)–N(2) [1.887(1) Å] distances and longer in comparison with Ge–O and Ge–N bonds in **1**. Chelate angles O(1)–Ge(1)–N(1) of 85.39(6)° and O(2)–Ge(1)–N(2) of 85.28(5)° are less than corresponding angles in **1**.

The second crystallographically independent molecule has a C_2 axis along the Ge–Cl bond, and both ligands are equal each to other. The resulting geometrical characteristics of the ligands are also intermediate between the dianion *o*-amidophenolate and the radical anion *o*-iminobenzosemiquinolate: the O–C bonds are 1.335(2) Å and the N–C bonds are 1.377(2) Å; the carbon ring also shows a quinoidtype of distortion.

The crystal structure of **5** indicates a charge distribution of (ISQ)(AP)GeCl. The structural equivalence of ligands can be explained by the presence of an overall molecular

orbital (MO) for both ligands with the formation of a delocalized valent state for the ligands. Additional evidence for this statement is the temperature-independent EPR spectrum of complex **5**, which indicates delocalization of the unpaired electron over two *o*-iminoquinonato ligands. A spin- and dipole-allowed LLCT (ligand-to-ligand charge transfer) between the group MOs of these ligands probably corresponds to the low-energy band (2300 nm) in NIR spectrum.

The molecule in the crystal of complex **4** contains a tetrahedral germanium atom coordinated with three perfluorophenyl groups and a nonchelating *O*-coordinated *o*-aminophenolato ligand (Figure 5). There is no bonding between the Ge(1) and N(1) atoms [the Ge(1)···N(1) distance is 3.261(5) Å].

The six-membered carbon ring C(1)C(6) is undoubtedly aromatic with an average C–C bond length of 1.396 ± 0.008 Å. The O(1)–C(1) distance [1.395(5) Å] is typical for phenolato ligands, the N(1)–C(2) bond length is 1.420(5) Å – this is significantly shorter than the same type of bond, N(1)–C(28) [1.465(2) Å]. The length of the germanium-to-oxygen bond Ge(1)–O(1) is close to Ge–O bonds in the four-coordinate (AP)₂Ge and typical for covalent Ge^{IV}–O bonds.

As mentioned above, steric factors play an important role in obtaining Ge^{IV} derivatives from Ge^{II}. Therefore, it is of interest to estimate quantitatively the steric factors in the complexes investigated. For this purpose, we shall use a model of the ligand solid angles, which allows to calculate the saturation of the coordinating sphere of the metal by ligands.^[12] Our calculation for complexes 1 and 3-5 shows that the saturations of the coordinating sphere of germanium are 92.6(2), 95.0(2), 96.5(2) and 96.2(2)%, respectively. It should be noted that the given values are very high in comparison with analogous characteristics for lanthanide complexes [85.6(5)-89.6(2)%].^[13] Besides, the reason why thf does not coordinate germanium in 1 but coordinates the central atom in bis(o-amidophenolato) derivative (AP)₂Sn(thf)^[3] becomes obvious as a result of this calculation. The saturation of the coordinating sphere in (AP)₂-Sn(thf)^[3] without the thf molecule is 79.9(2)%; that is significantly less than that in 1 [92.6(2)%]. The coordination of the thf molecule in the (AP)₂Sn(thf) complex increases the saturation of the coordinating sphere up to 94.7(2)%, which is close to the analogous value in 1. Thus, the steric size of the thf molecule is approximately equal to 14%. Complex 1 does not have 14% free space in the coordinating sphere of the germanium atom. Therefore, we can conclude that nonbonding ligand-ligand interactions in the coordinating sphere of 1 prevent the coordination of the thf molecule.

Conclusions

In the present paper we have shown that bulky aryl-substituted *o*-iminoquinone can serve as a versatile ligand that can be used to synthesize both divalent and tetravalent ger-

FULL PAPER

Experimental Section

noquinone.

General Remarks: All reactants were reagent grade. Solvents were purified by following standard methods.^[14] 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone (imQ)^[15] and tris-(per-fluorophenyl)germane^[16] were prepared according to known procedures. All manipulations on complexes were performed in vacuo under conditions in which oxygen and moisture were excluded.

The infrared spectra of the complexes in the 4000–400 cm⁻¹ range were recorded in Nujol with a Specord M-80 spectrophotometer. NMR spectra were recorded in C_7D_8 (1, 2), C_6D_6 (3) or CDCl₃ (4) solution by using a "Bruker DPX-200" instrument with Me₄Si as internal standard.

The EPR spectrum of **5** was recorded with a Bruker ER 200 D-SRC spectrometer with an ER041 MR microwave bridge, ER 4105 DR double resonator and ER 4111 VT variable temperature unit. The g_i values were determined by using diphenylpicrylhydrazyl as the reference ($g_i = 2.0037$). HFC constants were obtained by simulation with the WinEPR SimFonia Software (Bruker).

(AP)₂Ge (1): A solution of the o-amidophenolatolithium derivative^[4] (0.8 g, 2 mmol) in hexane or thf (20 mL) was added to GeCl₄ (0.2 g, 1 mmol) in the same solvent (10 mL), and after that the reaction mixture turned colourless. The thf was evaporated, and the residue was redissolved in *n*-hexane and filtered. Compound 1 was obtained as colourless, air-sensitive crystals from the cooling hexane solution. Yield: 0.63 g, 0.76 mmol, 75.7%; m.p. 305 °C. ¹H NMR (200 MHz, C_7D_8 , 25 °C): δ = 0.16 (br. s, 6 H, CH₃ of *i*Pr), 0.88 (br. s, 6 H, CH₃ of *i*Pr), 1.14 (br. s, 6 H, CH₃ of *i*Pr), 1.22 (s, 18 H, tBu), 1.28 (br. s, 6 H, CH₃ of iPr), 1.63 (s, 18 H, tBu), 2.63 (br. s, 2 H, CH of *i*Pr), 3.83 (br. s, 2 H, CH of *i*Pr), 6.29 (d, J_{H,H} = 2.2 Hz, 2 H, CH-aromatic), 6.88-7.19 (m, 6 H, CH-aromatic), 7.08 (d, $J_{\text{H,H}}$ = 2.2 Hz, 1 H, CH-aromatic) ppm. IR (Nujol): \tilde{v} = 1583 (s), 1447 (w), 1413 (s), 1362 (m), 1330 (s), 1287 (m), 1268 (w), 1229 (m), 1209 (vs), 1178 (w), 1160 (w), 1113 (m), 1103 (m), 1053 (w), 1042 (w), 1026 (w), 985 (vs), 966 (s), 932 (w), 911 (w), 859 (m), 821 (s), 804 (s), 774 (w), 757 (s), 739 (w), 671 (w), 656 (w), 603 (m), 567 (m), 524 (w), 509 (w), 471 (w), 437 (m) cm⁻¹. $C_{52}H_{74}GeN_2O_2$ (831.80): calcd. C 75.09, H 8.97, Ge 8.73; found C 75.02, H 8.97, Ge 8.76.

Reaction of GeCl₂·Dioxane with Lithium *o*-**Iminosemiquinonate:** A solution of the *o*-amidophenolatolithium complex^[4] (0.8 g, 2 mmol) in toluene (20 mL) was treated with an equimolar quantity of imQ (0.76 g, 2 mmol) in the same solvent (20 mL). The reaction mixture turned dark blue, indicating the formation of the (*o*-iminosemiquinonato)lithium derivative. It was then added to GeCl₂·dioxane (0.46 g, 2 mmol) in toluene (10 mL), and the colour of the radical anion complex disappeared immediately. The product was separated from lithium chloride by filtration, recrystallized from *n*-hexane and identified as compound 1 by its ¹H NMR spectrum and melting point. Yield: 0.91 g, 1.1 mmol, 55.0%.

(AP)Ge (2): A solution of the *o*-amidophenolatolithium derivative^[4] (0.8 g, 2 mmol) in thf (20 mL) was added to GeCl₂·dioxane (0.46 g, 2 mmol) in thf (10 mL). The reaction mixture turned orange immediately; thf was evacuated, the residue was additionally dried in vacuo at 80 °C and distilled at 120 °C (5×10^{-3} mm) to give a red viscous resin. Yield: 0.74 g, 1.6 mmol, 81.8%. ¹H NMR (200 MHz, C_7D_8 , 25 °C): δ = 0.92 (d, $J_{H,H}$ = 6.9 Hz, 6 H, CH₃ of *i*Pr), 0.97 (d, J_{H,H} = 6.9 Hz, 6 H, CH₃ of *i*Pr), 1.27 (s, 9 H, *t*Bu), 1.73 (s, 9 H, tBu), 2.65 (sept., $J_{H,H}$ = 6.9 Hz, 2 H, CH of *i*Pr), 6.45 (d, $J_{H,H}$ = 2.1 Hz, 1 H, CH-aromatic), 7.10–7.20 (m, 3 H, CHaromatic), 7.24 (d, J_{H,H} = 2.1 Hz, 1 H, CH-aromatic) ppm. IR (Nujol): $\tilde{v} = 1594$ (w), 1575 (m), 1412 (m), 1378 (m), 1363 (w), 1331 (m), 1302 (m), 1257 (w), 1240 (m), 1220 (w), 1203 (w), 1179 (w), 1164 (w), 1115 (w), 1103 (w), 1056 (w), 1041 (w), 1028 (w), 994 (s), 968 (w), 936 (m), 911 (w), 886 (w), 860 (m), 822 (w), 802 (s), 769 (m), 742 (w), 721 (s), 699 (w), 658 (w), 620 (w), 594 (m), 556 (m), 525 (m), 508 (w), 462 (w), 425 (w) cm⁻¹. $C_{26}H_{37}GeNO$ (452.22): calcd. C 69.05, H 8.25, Ge 16.06; found C 68.99, H 8.25, Ge 16.10.

Reaction of imQ with 2: The initially wine-red *o*-iminoquinone (imQ) (0.76 g, 2 mmol) suspension in thf (20 mL) was added to (*o*-amidophenolato)germanium(II) (**2**) (0.9 g, 2 mmol) in the same solvent (20 mL). The reaction mixture turned colourless. The product was recrystallized from *n*-hexane and identified as compound **1** by its ¹H NMR spectrum and melting point. Yield: 1.12 g, 1.35 mmol, 67.3%.

(AP)(APH)GeCl (3): Bis(o-amidophenolato)germanium(IV) (1) (0.83 g, 1 mmol) was dissolved in thf (20 mL) and exposed to anhydrous HCl obtained in a separate ampoule from NaCl (0.058 g, 1 mmol) and H₂SO₄ (1 mL). When gas evolution stopped, the thf solution was frozen to condense gaseous HCl, the ampoule was closed, and the solution was warmed. While warming, the reaction mixture turned brown, thf was evaporated and the residue was recrystallized from n-hexane. Complex 3 was obtained as lightbrown, nearly colourless crystals. Yield: 0.52 g, 0.545 mmol, 54.5%; m.p. 205 °C. ¹H NMR (200 MHz, C₆D₆, 25 °C): δ = 0.61 (d, J_{H,H} = 6.7 Hz, 3 H, CH₃ of *i*Pr), 1.04 (s, 9 H, *t*Bu), 1.13 (d, $J_{H,H}$ = 6.7 Hz, 3 H, CH₃ of *i*Pr), 1.18 (d, $J_{H,H}$ = 6.7 Hz, 3 H, CH₃ of *i*Pr), 1.19 (d, $J_{H,H}$ = 6.7 Hz, 6 H, CH₃ of *i*Pr), 1.19 (s, 9 H, *t*Bu), 1.20 (s, 9 H, tBu), 1.33 (d, $J_{H,H}$ = 6.7 Hz, 3 H, CH₃ of *i*Pr), 1.35 (d, $J_{\rm H,H}$ = 6.7 Hz, 3 H, CH₃ of *i*Pr), 1.45 (s, 9 H, *t*Bu), 1.56 (d, $J_{\rm H,H}$ = 6.7 Hz, 3 H, CH₃ of *i*Pr), 2.78 (sept., $J_{H,H}$ = 6.7 Hz, 1 H, CH of *i*Pr), 3.32 (sept., $J_{H,H}$ = 6.7 Hz, 1 H, CH of *i*Pr), 3.38 (sept., $J_{H,H}$ = 6.7 Hz, 1 H, CH of *i*Pr), 3.94 (sept., $J_{H,H}$ = 6.7 Hz, 1 H, CH of *i*Pr), 6.44 (d, $J_{H,H}$ = 2.2 Hz, 1 H, CH-aromatic), 6.65 (d, $J_{H,H}$ = 2.0 Hz, 1 H, CH-aromatic), 6.96 (d, $J_{H,H}$ = 2.2 Hz, 1 H, CH-aromatic), 7.08 (s, 1 H, NH), 7.11-7.19 (m, 2 H, CH-aromatic), 7.32 (d, $J_{H,H}$ = 2.0 Hz, 1 H, CH-aromatic), 7.25–7.44 19 (m, 4 H, CHaromatic) ppm; assignment of NMR signals was defined more exactly by using 2D COSY NMR spectroscopy. IR (Nujol): $\tilde{v} = 3262$ (s), 1579 (s), 1445 (w), 1416 (s), 1362 (m), 1334 (m), 1302 (w), 1292 (m), 1268 (w), 1251 (s), 1233 (m), 1211 (s), 1172 (m), 1118 (m), 1102 (w), 1052 (w), 1042 (m), 1028 (w), 967 (s), 966 (w), 942 (w), 931 (w), 911 (w), 877 (m), 846 (vs), 831 (w), 819 (w), 801 (m), 792 (w), 766 (w), 757 (s), 733 (m), 711 (w), 684 (w), 658 (m), 648 (w), 605 (m), 682 (m), 562 (w), 538 (w), 525 (w), 514 (w), 462 (w), 444 (w), 428 (m), 405 (w) cm⁻¹. $C_{58}H_{89}ClGeN_2O_2$ (954.43): calcd. C 72.99, H 9.40, Cl 3.71, Ge 7.61; found C 72.77, H 9.56, Cl 3.84, Ge 7.65.

(APH)Ge^{IV}(C₆F₅)₃ (4): The wine-red suspension of imQ (1 g, 2.6 mmol) in thf (20 mL) was added to a $(C_6F_5)_3$ GeH (0.63 g, 2.6 mmol) solution in the same solvent (10 mL). The colour of the reaction mixture changed to light brown. The solvent was evaporated, and the residue was recrystallized from a *n*-hexane/CH₂Cl₂ mixture as white air-stable crystals of 4 Yield: 1.41 g, 2.26 mmol,



86.9%; m.p. 213 °C. ¹H NMR (200 MHz, CDCl₃, 25 °C): δ = 0.85 (d, $J_{H,H}$ = 6.8 Hz, 6 H, CH₃ of *i*Pr), 0.99 (s, 9 H, *t*Bu), 1.05 (d, $J_{H,H}$ = 6.8 Hz, 6 H, CH₃ of *i*Pr), 1.25 (s, 9 H, *t*Bu), 2.80 (sept., $J_{H,H}$ = 6.8 Hz, 2 H, CH of *i*Pr), 5.63 (s, 1 H, NH), 5.80 (d, $J_{H,H}$ = 2.2 Hz, 1 H, CH-aromatic), 6.65 (d, $J_{H,H}$ = 2.2 Hz, 1 H, CH-aromatic), 7.05–7.24 (m, 3 H, CH-aromatic) ppm. IR (Nujol): \tilde{v} = 3386 (s), 1646 (s), 1597 (w), 1580 (m), 1519 (s), 1415 (m), 1384 (s), 1309 (m), 1290 (s), 1243 (w), 1221 (m), 1204 (m), 1183 (m), 1161 (m), 1147 (w), 1109 (m), 1086 (vs), 1017 (m), 976 (vs), 936 (m), 914 (w), 888 (w), 862 (m), 833 (s), 802 (m), 771 (m), 748 (vs), 684 (w), 651 (w), 620 (s), 601 (w), 585 (w), 572 (w), 532 (w), 501 (m), 460 (m) cm⁻¹. C₄₄H₃₈F₁₅GeNO (954.39): calcd. C 55.37, H 4.01, F 29.86, Ge 7.61; found C 55.29, H 3.99, F 29.87, Ge 7.65.

(AP)(ISQ)GeCl (5): Aminophenolate 3 (0.5 g, 0.6 mmol) was dissolved in acetone (15 mL), and the solution was placed in open air. The colour of reaction mixture slowly turned to dark green. Dark crystals of 5 formed as the solvent evaporated. Yield: 0.29 g, 0.35 mmol, 58.5%; m.p. 244 °C. IR (Nujol): $\tilde{v} = 1719$ (w), 1640 (m), 1573 (s), 1522 (w), 1447 (s), 1420 (w), 1361 (m), 1338 (w), 1322 (w), 1291 (m), 1257 (w), 1242 (w), 1223 (w), 1201 (m), 1169 (m), 1103 (m), 1057 (w), 1041 (w), 1030 (w), 998 (s), 935 (w), 912 (w), 894 (w), 855 (m), 829 (m), 802 (s), 771 (m), 757 (w), 727 (m), 706 (w), 685 (w), 654 (w), 611 (w), 600 (w), 557 (w), 541 (w), 528 (w), 508 (w), 433 (w) cm⁻¹. NIR (Nujol): ca. 2300 nm. C₅₂H₇₄ClGeN₂O₂ (867.25): calcd. C 72.02, H 8.60, Cl 4.09, Ge 8.38; found C 71.97, H 8.58, Cl 4.12, Ge 8.42.

X-ray Crystallographic Study of 1, 3, 4 and 5: Intensity data for 1, 3, 4 and 5 were collected at 100 K with a Smart Apex diffractometer with graphite monochromated Mo- K_{α} radiation (λ = 0.71073 Å) in the ϕ - ω scan mode ($\omega = 0.3^{\circ}$, 10 s on each frame). The intensity data were integrated by the SAINT program.^[17] SADABS^[18] was used to perform area-detector scaling and absorption corrections. The structures of 1 and 3 were solved by the Patterson method and those of 4 and 5 were solved by direct methods and were refined on F^2 by using all reflections with the SHELXTL package.^[19] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of complexes 1, 3 (except H atoms in the solvate hexane molecule) and 5 (except the H atoms for one tert-butyl group) were found from Fourier synthesis and refined isotropically. Hydrogen atoms in 4 were placed in calculated positions and refined in the "riding-model" $[U_{iso}(H) = 1.5U_{eq}(C)$ in CH₃ groups and $U_{iso}(H) = 1.2U_{eq}(C)$ in other ligands]. In complex 4 one of the tBu groups is disordered in two positions. Selected bond lengths and angles for 1, 3, 4 and 5 are given in Table 1. Table 2 summarizes the crystal data and some details of data collection and refinement for these complexes.

CCDC-645244, 661897, 661898, 661899 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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