Synthesis and Structural Characterization of a Gallium(III) Bis(selenoureato) Complex

Anja Molter and Fabian Mohr

Fachbereich C – Anorganische Chemie, Bergische Universität Wuppertal, Gaußstr. 20, 42119 Wuppertal, Germany

Reprint requests to Prof. Dr. Fabian Mohr.
Fax: +49 202 439 3053. E-mail: fmohr@uni-wuppertal.de

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In an attempt to prepare the tris(selenoureato)gallium(III) complex [Ga(4-$O_2NC_6H_4C(O)NC(Se)NEt_2)_3$] from the reaction of the nitro-substituted acylselenourea 4-$O_2NC_6H_4C(O)NHC(Se)NEt_2$ with [$Ga(NO_3)_3$] in EtOH we obtained a crystalline compound from a CH_2Cl_2 solution which was identified as the bis(selenoureato)gallium(III)chlorido complex [GaCl(4-$O_2NC_6H_4C(O)NC(Se)NEt_2)_2$] by single-crystal X-ray diffraction. This compound is a rare example of a metal complex containing chelating selenoureato ligands in a *trans* arrangement.

Key words: Acylselenourea, Chelate Ligands, Gallium(III), X-Ray Structure, Ligand Exchange

Introduction

Acylselenoureas of the type $ArC(O)NHC(Se)NR_2$ were first reported in 1937 by I. B. Douglass [1]. More than 30 years later, the group of L. Beyer showed that such selenoureas readily react with metal salts to form chelate complexes. In these, the deprotonated selenoureato unit coordinates to the metal through both the oxygen and selenium atoms (Fig. 1) [2].

Over the years the group of Beyer and others have reported spectroscopic and structural studies of metal complexes with various selenourea ligands. While most of this work has focused on copper(II) and nickel(II) bis(selenoureato) compounds, there are also a few examples of structural studies of main group metal derivatives including those containing Tl [3], In [4] and Pb [5, 6]. More recently several groups have reported the use of Pb and Cd selenoureato derivatives as single-source precursors for PbSe and CdSe nanomaterials [6 – 10]. Our group has begun a detailed investigation of the structures and applications of transition metal complexes containing selenoamide derivatives including selenoureas [11 – 19]. During our investigation we were surprised at the lack of information on main group metal compounds containing such selenoamide ligands. In extension of our work with In, Sb, Bi, and Sn complexes containing selenium ligands [16, 20], we report here a preliminary result of an unusual gallium(III)chlorido complex that we obtained adventitiously in an attempt to prepare the tris(selenoureato) derivative.

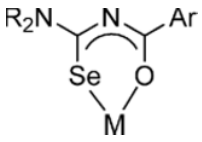


Fig. 1. Schematic illustration of an acylselenoureato metal complex.

Results and Discussion

Heating an ethanolic solution of [$Ga(NO_3)_3$] with 4-$O_2NC_6H_4C(O)NHC(Se)NEt_2$ in a 1 : 3 molar ratio resulted in a yellow, viscous material contaminated with a black amorphous powder, probably elemental Se. Once the black powder was separated, different products crystallised out of the filtrate, depending on the solvent used: Colourless crystals of the known ethyl ester 4-$O_2NC_6H_4C(O)OEt$ [21] were obtained by slow evaporation of an EtOH solution. However, when the viscous residue from a different experiment was dissolved in CH_2Cl_2 and filtered, a few yellow crystals deposited from the filtrate after some time. The ^1H and ^{13}C NMR spectra of a solution of these crystals showed signals consistent with the presence of a deprotonated selenourea, *e. g.* the signal for the NH proton was absent. Furthermore, the chemical shifts of the resonances due to the C – O and C – Se carbon atoms in the ^{13}C NMR spectrum were considerably different from those of the selenourea itself. Unfortunately, there was not enough material to record a ^{77}Se NMR spectrum. Given that with this spectroscopic data alone we could not determine the identity of the product, we carried out an X-ray diffraction study of the crystals.

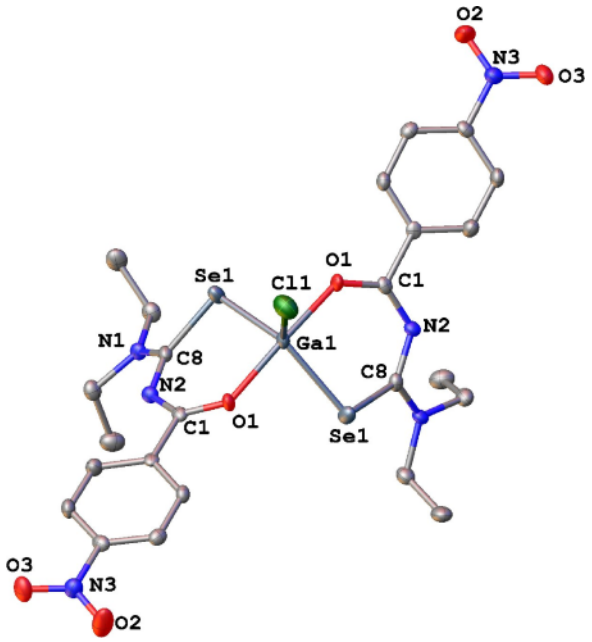


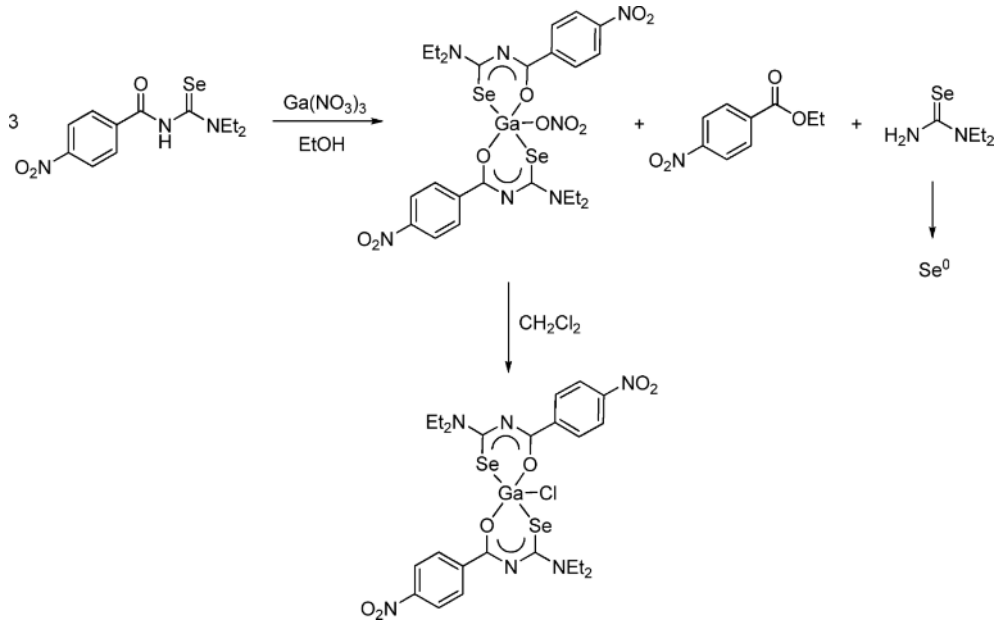
Fig. 2 (color online). Molecular structure of [GaCl(4-$O_2NC_6H_4C(O)NC(Se)NEt_2)_2$] in the solid state. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å); primed atoms are related to the unprimed ones by a crystallographic two-fold axis: Ga1 – Se1 2.3939(5), Ga1 – O1 2.031(2), Ga1 – Cl1 2.2118(17), Se1 – C8 1.912(3), O1 – C1 1.267(4), C8 – N2 1.347(4), C1 – N2 1.315(4). Selected bond angles (deg): Se1 – Ga1 – Se1* 131.91(3), O1 – Ga1 – O1* 171.48(15), O1 – Ga1 – Se1 92.32(6), Cl1 – Ga1 – Se1 114.046(17).

The molecular structure of the compound is shown in Fig. 2.

The yellow crystals turned out not to be the expected tris(selenoureato)gallium(III) complex, but rather a bis(selenoureato)gallium(III)chlorido complex. The molecule consists of two symmetry-equivalent, deprotonated selenourea molecules coordinating to the gallium atom through the oxygen and selenium atoms; the chloride ligand completes the coordination sphere about the gallium centre. Overall, the coordination geometry around the metal atom can be described as trigonal bipyramidal (tbp): the two selenium atoms and the chloride ligand form the equatorial triangle whilst the two oxygen atoms are located at the top and bottom of the bipyramid. Thus, the O – Ga – O* angle is almost linear (*ca.* 171°), and the Se – Ga – Se* angle is about 132°, close to the 120° expected for the tbp configuration. The six-membered metallacyclic rings are only slightly distorted from planarity, the Se atoms being twisted above the Ga – O – C planes. The Ga – Se distances (2.3939(5) Å) are slightly shorter than those observed in the cationic Ga(III) selenosemicarbazonato complex $[Ga\{pyC(Me)NNC(Se)NMe_2\}_2]^+$ (Ga – Se = 2.4908(6) Å) reported by Kowol [22]. The Ga – Cl bond (2.2118(17) Å) is longer than that observed in $[GaCl_3(SeMe_2)]$ [23], in which the average Ga – Cl distance is 2.15 Å, but rather similar to that reported for [GaCl{PhC(S)CHC(O)Ph}$_2$] (2.193(3) Å) [24]. Apart from the tris(selenoureato)indium(III) complex $[In(PhC(O)NC(Se)NEt_2)_3]$ reported by Schuster [4], the compound shown here is the only other known Group III metal selenoureato complex. Furthermore, this compound is a rare example of a metal complex containing chelating selenoureato ligands arranged in a *trans* fashion. The only other cases with such *trans* arrangement of the selenoureato ligands are the Zn(II) and Pb(II) bis(chelates) containing deprotonated $PhC(O)NHC(Se)NEt_2$ [5, 25].

The obvious question is of course how this chlorido complex was generated. We believe that the species initially formed is probably a bis(selenoureato) gallium(III)nitrato complex. Indirect evidence for this is the isolation of the 4-nitrophenyl ester (see above). Two equivalents of selenourea react with the gallium(III) nitrate leaving one equivalent of selenourea which under the acidic conditions (protons are released during the reaction) decomposes to the ethyl ester and the selenourea $H_2NC(Se)NEt_2$. This selenourea is likely to be thermally unstable and may thus decompose in refluxing EtOH to eventually produce elemental Se. Once the bis(selenoureato)gallium(III)nitrato species is left to stand in a chlorinated solvent, one of the selenoureato ligands or the nitrato ligand is slowly displaced by a chlorido ligand. This displacement might be favourable, given that the steric bulk of three selenoureato ligands around the gallium centre is expected to be quite significant. The resulting bis(selenoureato)gallium(III)chlorido species is less soluble and thus crystallises out of the solution after a period of time. Scheme 1 summarises our proposed reaction scheme leading to the observed products.

Work by Nöth has demonstrated that the sodium salt of the structurally not too dissimilar benzoyl(thiobenzoyl)methane, $Na^+[PhC(S)CHC(O)Ph]^-$, reacts with $GaCl_3$ irrespective of the molar ra-



Scheme 1.

tio used to afford the galliumchlorido(III) species [GaCl{PhC(S)CHC(O)Ph}$_2$] containing two deprotonated ligands [24]. Their interpretation for this observation and also for the fact that the chlorido ligand in the compound is kinetically inert was based on steric effects. It appears that with our selenourea ligand the same trend is observed. Efforts are now underway to develop a rational synthesis for this compound starting from $GaCl_3$, and we are also interested in investigating the compound as a possible single-source precursor for GaSe nanomaterials.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a 600 MHz Bruker Avance III spectrometer. Chemical shifts are quoted relative to external $SiMe_4$ (^{1}H, ^{13}C). The selenourea 4-$O_2NC_6H_4C(O)NHC(Se)NEt_2$ was prepared according to the method by Douglass [1] from 4-$O_2NC_6H_4C(O)Cl$, KSeCN and Et_2NH. All other chemicals and solvents (HPLC grade) were from commercial sources and used as received.

Attempted synthesis of [Ga(4-$O_2NC_6H_4C(O)NC(Se)NEt_2)_3$]

A mixture of [$Ga(NO_3)_3$] (0.031 g, 0.12 mmol) and 4-$O_2NC_6H_4C(O)NHC(Se)NEt_2$ (0.120 g, 0.37 mmol) in ethanol (20 mL) was heated to reflux for *ca.* 45 min. The orange solution was concentrated in vacuum to give a yellow, viscous residue contaminated with a black powder. This material was taken up in CH_2Cl_2, passed through Celite, and on standing over a period of several days deposited a few yellow crystals, which were used for the subsequent char-

Table 1. Crystal structure data for [GaCl(4-$O_2NC_6H_4C(O)NC(Se)NEt_2)_2$].

Formula	$C_{24}H_{28}ClGaN_6O_6Se_2$
M_r	759.61
Crystal size, mm^3	0.03 × 0.05 × 0.06
Crystal system	monoclinic
Space group	*C*2/*c*
a, Å	28.6524(15)
b, Å	6.9835(4)
c, Å	14.0605(7)
β, deg	95.452(5)
V, Å^3	2800.7(3)
Z	4
D_{calcd}, g cm^{-3}	1.80
μ(Mo K_α), mm^{-1}	3.7
F(000), e	1512
hkl range	±36, −9 to 8, −13 to 19
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.680
Refl. measured / unique / R_{int}	6547 / 3258 / 0.0399
Param. refined	184
$R(F)$ / $wR(F^2)$[a] (all refls.)	0.0742 / 0.0652
GoF (F^2)[b]	0.843
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.85 / −0.55

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$; [b] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

acterisation. – ^{1}H NMR (600 MHz, CD_2Cl_2): $\delta = 1.26$ (t, $J = 7.1$ Hz, 12 H, NCH_2CH_3), 3.54 (br. s, 4 H, NCH_2), 3.89 (br. s, 4 H, NCH_2), 8.23 (d, $J = 8.8$ Hz, 4 H, arom.), 8.29 (d, $J = 8.8$ Hz, 4 H, arom.). – ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2): $\delta = 11.5$ (NCH_2CH_3), 12.7 (NCH_2CH_3), 44.0 (NCH_2CH_3), 51.3 (NCH_2CH_3), 123.4, 130.6, 136.0, 150.5 (arom.), 164.6 (C–O), 170.8 (C–Se). When the residue was taken up in EtOH and passed through Celite, colourless crystals of 4-$O_2NC_6H_4C(O)OEt$ deposited in the filtrate upon slow evaporation.

X-Ray structure determination

Diffraction data were collected at 150 K using an Oxford Diffraction Gemini E Ultra diffractometer, equipped with an EOS CCD area detector and a four-circle kappa goniometer. For the data collection graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) was used. Data integration, scaling and empirical absorption correction was carried out using the CrysAlisPro program package [26]. The structure was solved using Direct Methods and refined by full-matrix least-squares against F^2. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealised positions and refined using the riding model. All calculations were carried out using the program Olex2 [27]. Important crystallographic data and refinement details are summarised in Table 1.

CCDC 912855 contains 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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