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

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In an attempt to prepare the tris(selenourea)gallium(III) complex $[\text{Ga}(4\text{-O}_2\text{NC}_6\text{H}_4\text{C(O)NHC(Se)NEt}_2)_3]$ from the reaction of the nitro-substituted acylselenourea $4\text{-O}_2\text{NC}_6\text{H}_4\text{C(O)NHC(Se)NEt}_2$ with $[\text{Ga(NO}_3)_3]$ in EtOH we obtained a crystalline compound from a CH$_2$Cl$_2$ solution which was identified as the bis(selenourea)gallium(III)chlorido complex $[\text{GaCl}(4\text{-O}_2\text{NC}_6\text{H}_4\text{C(O)NHC(Se)NEt}_2)_2]$ by single-crystal X-ray diffraction. This compound is a rare example of a metal complex containing chelating selenourea ligands in a trans arrangement.

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

Introduction

Acylselenoureas of the type ArC(O)NHCNR$_2$ 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 selenourea 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(selenourea) compounds, there are also a few examples of structural studies of main group metal derivatives including those containing TI [3], In [4] and Pb [5, 6]. More recently several groups have reported the use of Pb and Cd selenourea derivatives as single-source precursors for PbSe and CdSe nano-

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

materials [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 selenourea 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(selenourea) derivative.

Results and Discussion

Heating an ethanolic solution of $[\text{Ga(NO}_3)_3]$ with $4\text{-O}_2\text{NC}_6\text{H}_4\text{C(O)NHC(Se)NEt}_2$ 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 crystallized out of the filtrate, depending on the solvent used: Colourless crystals of the known ethyl ester $4\text{-O}_2\text{NC}_6\text{H}_4\text{C(O)OEt}$ [21] were obtained by slow evaporation of an EtOH solution. However, when the viscous residue from a different experiment was dissolved in CH$_2$Cl$_2$ and filtered, a few yellow crystals deposited from the filtrate after some time. The $^1$H 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.
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 selenourea complex. Furthermore, this compound is a rare example of a metal complex containing chelating selenourea ligands arranged in a trans fashion. The only other cases with such trans arrangement of the selenourea ligands are the Zn(II) and Pb(II) bis(chelates) containing deprotonated PhC(O)NH(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 selenourea ligands or the nitrato ligand is slowly displaced by a chlorido ligand. This displacement might be favourable, given that the steric bulk of three selenourea 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 Nőth 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-
tio used to afford the galliumchlorido(III) species [GaCl(PhC(S)CHC(O)Ph)₂] containing two deproto-
nated ligands [24]. Their interpretation for this obser-
vation 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 GaCl₃, and we are also interested in investigating
the compound as a possible single-source precursor for
GaSe nanomaterials.

Experimental Section

¹H and ¹³C NMR spectra were recorded on a 600 MHz
Bruker Avance III spectrometer. Chemical shifts are quoted
relative to external SiMe₄ (¹H, ¹³C). The selenourea 4-
O₂NC₆H₄C(O)NHC(Se)NEt₂ was prepared according to the
method by Douglass [1] from 4-O₂NC₆H₄C(O)Cl, KSeCN
and Et₂NH. All other chemicals and solvents (HPLC grade)
were from commercial sources and used as received.

Attempted synthesis of [Ga(4-O₂NC₆H₄C(O)NC(Se)NEt₂)₃]

A mixture of [Ga(NO₃)₃] (0.031 g, 0.12 mmol) and
4-O₂NC₆H₄C(O)NHC(Se)NEt₂ (0.120 g, 0.37 mmol) in
ethanol (20 mL) was heated to reflux for ca. 45 min. The or-
ange solution was concentrated in vacuum to give a yellow,
viscous residue contaminated with a black powder. This ma-
terial was taken up in CH₂Cl₂, 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-O₂NC₆H₄C(O)NC(Se)NEt₂)₂].

<table>
<thead>
<tr>
<th>Formula</th>
<th>C₂₄H₂₈ClGaN₆O₆Se₂</th>
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<tbody>
<tr>
<td>Mr</td>
<td>759.61</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
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<tr>
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<td>C2/c</td>
</tr>
<tr>
<td>a, Å</td>
<td>28.6524(15)</td>
</tr>
<tr>
<td>b, Å</td>
<td>6.9835(4)</td>
</tr>
<tr>
<td>c, Å</td>
<td>14.0605(7)</td>
</tr>
<tr>
<td>β, deg</td>
<td>95.452(5)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>2800.7(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>D_calcd, g cm⁻³</td>
<td>1.80</td>
</tr>
<tr>
<td>µ (MoKα), mm⁻¹</td>
<td>3.7</td>
</tr>
<tr>
<td>F(000), e</td>
<td>1512</td>
</tr>
<tr>
<td>hkl range</td>
<td>±36, −9 to 8, −13 to 19</td>
</tr>
<tr>
<td>(sinθ/λ) max, Å⁻¹</td>
<td>0.680</td>
</tr>
<tr>
<td>R(f) / wR(F²) (all refls.)</td>
<td>0.0742 / 0.0652</td>
</tr>
<tr>
<td>GOF (F²)</td>
<td>0.843</td>
</tr>
<tr>
<td>Đρ(max / min), e Å⁻³</td>
<td>0.85 / −0.55</td>
</tr>
</tbody>
</table>

[a] R(F) = Σ||Fo|−|Fc||/Σ|Fo|;  wR(F²) = [Σw(F² − F²c)²/Σw(F²c)²]¹/²,  w = (σ²(F²) + (AP)² + BP)⁻¹,  where  P = (Max(F²c, 0) + 2F²c²)/3; b GOF = [Σw(F² − F²c)²/(n(param)− n(param))⁻¹/². 

Scheme 1.
acterisation. $^1$H NMR (600 MHz, CD$_2$Cl$_2$): $\delta$ = 1.26 (t, $J$ = 7.1 Hz, 12 H, NCH$_2$CH$_3$), 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$_2$Cl$_2$): $\delta$ = 11.5 (NCH$_2$CH$_3$), 12.7 (NCH$_2$CH$_3$), 44.0 (NCH$_2$CH$_3$), 51.3 (NCH$_2$CH$_3$), 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$_2$NC$_4$H$_4$C(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 Mo $K\alpha$ radiation ($\lambda$ = 0.71073 Å) was used. Data integration, scaling and empirical absorption correction was carried out using the CRYSTALS 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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[26] CRYSTALS program package [26].