1-1-1997

**N-Methylbenzothiazole-2(3H)-selone, C₈H₇NSSe**

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The crystal structure of N-methyl-1,3-benzothiazole-2(3H)-selone (mbts) has just been used as a ligand both in the complexes [(mbts)TeBr2] and [(mbts)IBrBr, (4), and (mbts)IBrBr, (5) (Cristiani et al., 1994)], but the structure of the ligand itself has not yet been studied. Looking at the chemical structure of mbts, we might expect that it is good at delocalizing the positive charge owing to the resulting aromatic structure upon coordination.

**Comment**

Recently, we have shown (Rudd, Lindeman & Husebye, 1996) that the trans influence of chalcogen-containing ligands in hypervalent three-coordinate complexes of TeII can be modified significantly depending on the ability of the rest of the ligand (apart from the coordinating chalcogen atom) to accept/delocalize positive charge, owing to the following resonance:

\[
X^-\text{Te}(\text{Ar})\text{Y}^+L^-\text{X}^-\text{Te}(\text{Ar})\text{Y}^+L\leftrightarrow (a)
\]

\[
X^-\text{Te}(\text{Ar})\text{Y}^+L^-\text{X}^-\text{Te}(\text{Ar})\text{Y}^+L\leftrightarrow (b)
\]

\[
X^-\text{Te}(\text{Ar})\text{Y}^+L^-\text{X}^-\text{Te}(\text{Ar})\text{Y}^+L\leftrightarrow (c)
\]

(most often, \(X = \) a halogen, \(\text{Ar} = \) phenyl, \(Y = \) a chalcogen, \(L = \) the organic remainder of the ligand \(Y=L\) and ‘:’ denotes a lone pair). Moreover, we have demonstrated (Rudd, Lindeman & Husebye, 1997) that the same hypervalent three-center four-electron bonding scheme (Wiebenga, Havinga & Boswijk, 1961; Foss, 1962; Alcock, 1972) can be applied to isoelectronic hypervalent complexes of two-coordinate \(I^1\):

\[
X^-I:^Y\leftrightarrow L^-\leftrightarrow X^-I:^Y\leftrightarrow L^-\leftrightarrow X^-I^-L^+
\]

(most often, \(X = I\) or \(\text{Br}\), \(Y = S\) or \(\text{Se}\), and \(L = \) the organic remainder of the ligand). N-Methylbenzothiazole-2(3H)-selone (mbts), (1), has just been used as a ligand both in TeII and SeII complexes [(mbts)TePhBr, (2) (Rudd, Lindeman & Husebye, 1996), and (mbts)Se2+ (Adamo et al., 1996)], and in \(I^1\) complexes [(mbts)I^1]^+ (3) (Demartin et al., 1993), (mbts)I2 (4), and (mbts)IBrBr, (5) (Cristiani et al., 1994), but the structure of the ligand itself has not yet been studied. Looking at the chemical structure of mbts, we might expect that it is good at delocalizing the positive charge owing to the resulting aromatic structure upon coordination.

Nevertheless, the effect of the organic remainder of the ligand upon the trans influence of Se is rather small. For instance, mbts has a weaker trans influence than selenourea (Rudd, Lindeman & Husebye, 1996). In order to examine the reasons for this limited effect, we undertook the X-ray structural investigation of (1).
The molecular geometry of the non-coordinated molecule, (1), is compared with that of the Te- and I-coordinated mbts ligands in Table 1. Unfortunately, only a few accurate bond lengths of the non-coordinated Se≡C double bond are known. A recent precise work focusing on the similar 1,3-oxazolidine-2-selenones (Jie Peng et al., 1994) has been published where the Se≡C bond length varies in the range 1.798–1.843 Å [average 1.822 (17) Å]. This corresponds well with our data [1.814 (7) and 1.820 (7) Å; average 1.817 Å] for the non-coordinated mbts molecule in (1).

Elongation of this bond during coordination is significant. The Se≡C bond lengths of 1.845 (5) and 1.858 (5) Å (average 1.851 Å) found in the symmetrical hypervalent 11 complex (3) might be considered to have a bond order of one and a half in the case where the positive charge is completely accepted by the organic moiety of the two seleno ligands. This corresponds well with our data [1.822 (17) Å; see the resonance formula (b)] above. Indeed, we do not find many changes in the organic fraction of the mbts ligand upon coordination (Table 1). The positive charge is mostly localized on the S-C bond of ca 1.814 (7) and 1.820 (7) Å; average 1.817 Å] for the non-coordinated mbts molecule in (1).

Experimental

N-Methylbenzothiazole-2(3H)-selone was purchased from Aldrich and recrystallized from CH2Cl2 at 253 K as a mixture of two crystalline modifications, i.e. brown prisms and yellow plates. Only the former crystals became suitable for the X-ray structural investigation. A correction for decay of the sample was applied.

Crystal data

\[
\begin{array}{ll}
\text{C}_9\text{H}_7\text{NSSe} & \text{Mo Kα radiation} \\
M_1 = 228.17 & \lambda = 0.70696 \text{ Å} \\
\text{Monoclinic} & \text{Cell parameters from 24} \\
C_2/c & \text{reflections} \\
\alpha = 32.403 (6) \text{ Å} & \theta = 9.1–9.9° \\
b = 7.668 (2) \text{ Å} & \mu = 4.710 \text{ mm}^{-1} \\
c = 14.127 (3) \text{ Å} & T = 103 (2) \text{ K} \\
\beta = 109.20 (3)° & \text{Prism} \\
V = 3314.8 (13) \text{ Å}^3 & 0.10 \times 0.05 \times 0.05 \text{ mm} \\
Z = 16 & \text{Brown} \\
D_t = 1.829 \text{ Mg m}^{-3} & \\
D_m \text{ not measured} & \\
\end{array}
\]

Data collection

\[
\begin{array}{ll}
\text{Enraf–Nonius CAD-4} & 2331 \text{ reflections with} \\
diffactometer & I > 2σ(I) \\
\text{ω/2θ scans} & \theta_{\text{max}} = 26° \\
\text{Absorption correction:} & h = -39 \rightarrow 37 \\
\psi \text{ scan (North, Phillips} & k = 0 \rightarrow 9 \\
& \text{& Mathews, 1968)} \\
T_{\text{min}} = 0.625, T_{\text{max}} = 0.802 & l = 0 \rightarrow 17 \\
3240 \text{ measured reflections} & 3 \text{ standard reflections} \\
3240 \text{ independent reflections} & \text{frequency: 120 min} \\
& \text{intensity decay: 3.4%} \\
\end{array}
\]

Refinement

\[
\begin{array}{ll}
\text{Refinement on } F^2 & w = 1/[σ^2(F^2) + (0.072P)^2] \\
R[F^2 > 2σ(F^2)] = 0.0529 & + 5.14P] \\
wR(F^2) = 0.1648 & \text{where } P = (F^2 + 2F_C^2)/3
\end{array}
\]
Table 1. Comparison of average geometric parameters (Å, °) of the mbts molecule in structures (1)–(5)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N°</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>S1–C2–C9</td>
<td>1.87</td>
<td>1.85</td>
<td>1.87</td>
<td>1.85</td>
<td>1.89</td>
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<tr>
<td>S1–C2–N3</td>
<td>1.73</td>
<td>1.73</td>
<td>1.72</td>
<td>1.73</td>
<td>1.71</td>
</tr>
<tr>
<td>S1–C9–C4</td>
<td>1.34</td>
<td>1.33</td>
<td>1.34</td>
<td>1.33</td>
<td>1.36</td>
</tr>
<tr>
<td>C4–C5–C6</td>
<td>117.9</td>
<td>116.7</td>
<td>117.9</td>
<td>118.3</td>
<td>117.9</td>
</tr>
<tr>
<td>C4–N3–C10</td>
<td>121.9</td>
<td>122.4</td>
<td>121.8</td>
<td>121.7</td>
<td>121.4</td>
</tr>
<tr>
<td>C2–N3–C4</td>
<td>114.9</td>
<td>114.5</td>
<td>114.8</td>
<td>114.1</td>
<td>114.7</td>
</tr>
<tr>
<td>C7–C8–C9</td>
<td>1.37</td>
<td>1.38</td>
<td>1.39</td>
<td>1.38</td>
<td>1.39</td>
</tr>
<tr>
<td>C8–C9–C10</td>
<td>109.6</td>
<td>110.5</td>
<td>110.4</td>
<td>110.2</td>
<td>110.1</td>
</tr>
</tbody>
</table>

\( n = \text{number of independent structural mbts units.} \)

Refinement on \( F^2 \) for all reflections except for 31 with very negative \( F^2 \) \([-3\sigma(F^2)] \) or flagged by us for potential systematic errors.

Programs used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AV1002). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

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\( p \)-Nitrophenyl \( \alpha \)-D-Mannopyranoside

Ethanol Solvate

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(Received 10 November 1995; accepted 23 December 1996)

Abstract
The sugar moiety of the title compound, \( C_{12}H_{15}NO_8 \)-C\(_2\)H\(_5\)O\(_7\), has a \( \beta \)-C\(_1\) conformation. The nitrophenyl group adopts a planar conformation. The glycosidic linkage is \( \alpha \). The angle between the ‘best planes’ through the saccharide and aglycon residues is 71.5(1)°.

Comment
The ways in which the legume lectin Concanavalin A (Con A) binds to a series of saccharides consisting of a mannoside or glucoside group (saccharide residue) bonded to a second hydrophobic ring (aglycon residue) are currently being studied (Kanellopoulos et al., 1996). The title compound, the methanol solvate of \( p \)-nitrophenyl \( \alpha \)-d-mannopyranoside (\( \alpha \)-PNM), (I), a member of the series, binds to Con A with a high affinity. Its precise molecular structure determination was necessary for modelling the Con A–saccharide complexes.