

Marquette University
e-Publications@Marquette

Chemistry Faculty Research and Publications

Chemistry, Department of

1-1-1997

N-Methylbenzothiazole-2(3*H*)-selone,
 C_8H_7NSSe

Steinar Husebye
University of Bergen

Sergey V. Lindeman
Marquette University, sergey.lindeman@marquette.edu

Martin D. Rudd
University of Wisconsin - Fox Valley

Published version. *Acta Crystallographica Section C*, Vol. 53 (1997): 809-811. DOI. © 1997
International Union of Crystallography. Used with permission.
Sergey V. Lindeman was affiliated with Baylor University at the time of publication.

Data collection: *DIF4* (Stoe & Cie, 1990a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

The authors thank the EPSRC for provision of a four-circle diffractometer and an Earmarked Studentship (ICC).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1136). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Anderson, E. L., Casey, J. E., Greene, L. C., Lafferty, J. J. & Reiff, H. E. (1964). *J. Med. Chem.* **7**, 259–268.
 Blake, A. J., Hunter, G. A. & McNab, H. (1989). *J. Chem. Res.* (S), pp. 118–119; *J. Chem. Res.* (M), pp. 0921–0943.
 Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–108.
 Gero, A. (1954). *J. Org. Chem.* **19**, 1960–1970.
 Kirsch, G., Mieloszynski, J. L., Paquer, D. & Andrieu, C. G. (1983). *Recl. Trav. Chim. Pays-Bas*, **102**, 489–495.
 Sheldrick, G. M. (1995). *SHELXTL/PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Stoe & Cie (1990a). *DIF4*. *Diffractometer Control Program*. Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.
 Stoe & Cie (1990b). *REDU4*. *Data Reduction Program*. Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1997). **C53**, 809–811

N-Methylbenzothiazole-2(3*H*)-selone, C₃H₇NSSe

STEINAR HUSEBYE,^a SERGEY V. LINDEMAN^{b*} AND MARTIN D. RUDD^c

^aDepartment of Chemistry, University of Bergen, 41 Alle-gaten, N-5007 Bergen, Norway, ^bInstitute of Organoelement Compounds, 28 Vavilov Street, Moscow 117813, Russia, and ^cDepartment of Chemistry, Baylor University, Waco, Texas 76798-7348, USA. E-mail: sergey@bayou.uh.edu

(Received 30 July 1996; accepted 8 January 1997)

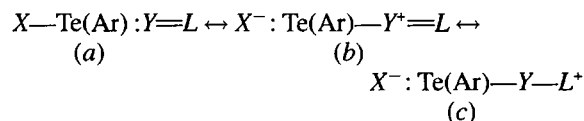
Abstract

The crystal structure of *N*-methyl-1,3-benzothiazole-2(3*H*)-selone (mbts) has been studied in order to estimate the changes in the molecular geometry of the mbts ligand upon coordination. Hypervalent complexes of mbts with Te^{II} and I^I have been studied by us previously. A significant elongation of the Se=C bond [from

1.817 (7) in mbts to 1.85–1.88 Å in the complexes] was found, but there were no significant changes in the other geometric parameters of the ligand. The only other bond-length decrease of note was for SeC—NMe [from 1.35 (1) in mbts to 1.32–1.34 Å in the complexes]. Thus, only the amino group takes part in electron redistribution upon coordination.

Comment

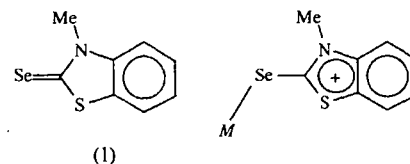
Recently, we have shown (Rudd, Lindeman & Husebye, 1996) that the *trans* influence of chalcogen-containing ligands in hypervalent three-coordinate complexes of Te^{II} can be modified significantly depending on the ability of the rest of the ligand (apart from the coordinating chalcogen atom) to accept/delocalize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



(most often, *X* = a halogen, *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^I:



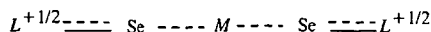
(most often, *X* = I or Br, *Y* = S or Se, and *L* = the organic remainder of the ligand). *N*-Methylbenzothiazole-2(3*H*)-selone (mbts), (1), has just been used as a ligand both in Te^{II} and Se^{II} complexes [(mbts)TePhBr, (2) (Rudd, Lindeman & Husebye, 1996), and (mbts)₄Se²⁺ (Adamo *et al.*, 1996)], and in I^I complexes [(mbts)₂I⁺·(I₃)⁻, (3) (Demartin *et al.*, 1993), (mbts)I₃, (4), and (mbts)IBrIBr, (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 complexation.



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-selones (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 I^I 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.



In the other mbts complexes investigated [(2), (4) and (5)], the Se—C bond is further lengthened [up to 1.880 (8) Å in (5)]. However, none of them reach the standard value for an ordinary conjugated C_{sp²}—Se bond length in tetraselenafulvalene [1.893 (13) Å; Allen *et al.*, 1987]. It is therefore suggested that the positive charge is mostly localized on the Se atom [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 S atom

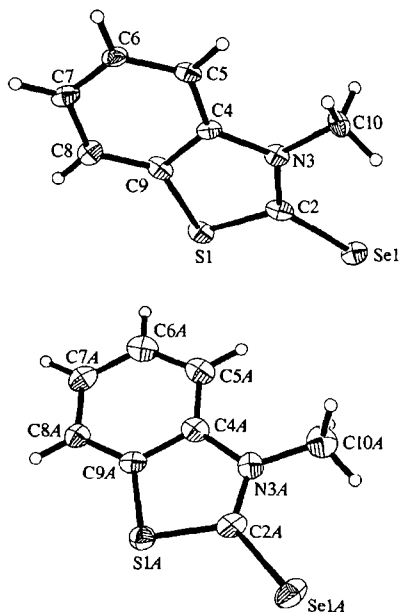


Fig. 1. Perspective view of the two symmetrically independent mbts molecules in the structure of (1) showing the labelling of non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

does not take part in such changes. Although the two S—C bond lengths differ in all these molecules [the S1—C2 bond of *ca* 1.72 Å is shorter than the S1—C9 bond of *ca* 1.74 Å; Table 1], they have not changed perceptibly during coordination and neither have the geometrical parameters of the benzene ring. The only bond length to change to a reasonable degree is C2—N3 [*ca* 1.35 Å in (1), *ca* 1.335 Å in (2)–(4) and *ca* 1.32 Å in (5); Table 1], which becomes a little closer to a double bond upon coordination. This corresponds to a partial delocalization of the positive charge accepted onto the N atom. As a result, we can say that the S atom in the mbts ligand does not take a significant part in the electron redistribution upon coordination and possibilities of electron delocalization in this ligand are limited mainly to the amino group. Thus, the aromatic resonance proposed is not reached and the ability of the mbts ligand to accept the positive charge in the hypervalent complexes investigated is weaker compared with selenourea derivatives.

Experimental

N-Methylbenzothiazole-2(3*H*)-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

C₈H₇NSSe
M_r = 228.17
 Monoclinic
 C2/*c*
a = 32.403 (6) Å
b = 7.668 (2) Å
c = 14.127 (3) Å
 β = 109.20 (3)°
V = 3314.8 (13) Å³
Z = 16
D_x = 1.829 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 24 reflections
 θ = 9.1–9.9°
 μ = 4.710 mm⁻¹
T = 103 (2) K
 Prism
 0.10 × 0.05 × 0.05 mm
 Brown

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω/2θ scans
 Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
T_{min} = 0.625, *T_{max}* = 0.802
 3240 measured reflections
 3240 independent reflections

2331 reflections with *I* > 2σ(*I*)
 θ_{max} = 26°
h = -39 → 37
k = 0 → 9
l = 0 → 17
 3 standard reflections
 frequency: 120 min
 intensity decay: 3.4%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.0529
wR(*F*²) = 0.1648

$w = 1/[\sigma^2(F_o^2) + (0.072P)^2 + 5.14P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.091$
3209 reflections
205 parameters
H atoms: riding and rotating model

$(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 1.403 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.379 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Comparison of average geometric parameters (Å , $^\circ$) of the mbts molecule in structures (1)–(5)

Compound	(1)	(3)	(4)	(2)	(5)
N^\dagger	2	2	3	2	1
Se1—C2	1.817	1.851	1.857	1.859	1.880
S1—C2	1.723	1.713	1.721	1.723	1.711
S1—C9	1.738	1.738	1.740	1.744	1.754
C2—N3	1.349	1.335	1.334	1.336	1.317
N3—C4	1.406	1.402	1.399	1.393	1.413
N3—C10	1.443	1.465	1.482	1.470	1.497
C4—C5	1.391	1.393	1.382	1.385	1.390
C4—C9	1.393	1.383	1.394	1.389	1.386
C5—C6	1.379	1.377	1.371	1.389	1.367
C6—C7	1.394	1.365	1.380	1.401	1.392
C7—C8	1.387	1.381	1.378	1.377	1.373
C8—C9	1.370	1.381	1.392	1.391	1.390
C2—S1—C9	92.7	91.3	91.1	90.9	90.7
Se1—C2—S1	122.1	123.9	124.7	124.3	124.5
Se1—C2—N3	127.3	124.2	123.4	123.5	122.6
S1—C2—N3	110.5	111.9	111.9	112.3	112.9
C2—N3—C4	114.9	114.5	114.8	114.1	114.7
C2—N3—C10	123.1	123.1	123.3	124.1	123.9
C4—N3—C10	121.9	122.4	121.8	121.7	121.4
N3—C4—C5	127.3	127.3	127.3	126.7	128.0
N3—C4—C9	112.3	111.7	111.5	112.4	111.2
C5—C4—C9	120.4	121.0	121.2	120.9	120.8
C4—C5—C6	117.9	116.7	117.9	118.3	117.0
C5—C6—C7	121.7	122.4	121.2	120.6	122.4
C6—C7—C8	119.7	121.0	121.9	120.8	120.9
C7—C8—C9	118.9	117.7	117.3	118.4	117.0
S1—C9—C4	109.6	110.7	110.6	110.3	110.6
S1—C9—C8	129.1	128.8	128.8	128.8	127.6
C4—C9—C8	121.3	121.1	120.5	120.9	121.8

$\dagger N$ = 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.

Program(s) 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

- Adamo, C., Demartin, F., Deplano, P., Devillanova, F. A., Isaia, F., Lelj, F., Lippolis, V., Lukes, P. & Mercuri, M. L. (1996). *J. Chem. Soc. Chem. Commun.* pp. 873–874.
- Alcock, N. W. (1972). *Adv. Inorg. Chem. Radiochem.* **15**, 1–58.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–S19.
- Cristiani, F., Demartin, F., Devillanova, F. A., Isaia, F., Lippolis, V. & Verani, G. (1994). *Inorg. Chem.* **33**, 6315–6324.
- Demartin, F., Deplano, P., Devillanova, F. A., Isaia, F., Lippolis, V. & Verani, G. (1993). *Inorg. Chem.* **32**, 3694–3699.
- Foss, O. (1962). *Acta Chem. Scand.* **16**, 779–780.

- Jie Peng, Barr, M. E., Ashburn, D. A., Odom, J. D., Dunlap, R. B. & Silks III, L. A. (1994). *J. Org. Chem.* **59**, 4977–4987.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst. A24*, 351–359.
- Rudd, M. D., Lindeman, S. V. & Husebye S. (1996). *Acta Chem. Scand.* **50**, 759–774.
- Rudd, M. D., Lindeman, S. V. & Husebye S. (1997). *Acta Chem. Scand.* In the press.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Wiebenga, E. H., Havinga, E. E. & Boswijk, K. H. (1961). *Adv. Inorg. Chem. Radiochem.* **3**, 133–169.

Acta Cryst. (1997). **C53**, 811–814

p-Nitrophenyl α -D-Mannopyranoside Ethanol Solvate

BOGOS AGIANIAN,^a ANASTASSIS PERRAKIS,^b PANAGIOTIS N. KANELLOPOULOS,^a BERNARD SHELDRIK^c AND STAVROS J. HAMODRAKAS^d

^aEuropean Molecular Biology Laboratory (EMBL), Meyerhofstrasse 1, 69117 Heidelberg, Germany,

^bNetherlands Cancer Institute (NKI), Department H2, Plesmanlaan 121, 1066 CX Amsterdam, The Netherlands,

^cDepartment of Biophysics, University of Leeds, Leeds LS2 9JT, England, and ^dDepartment of Biology, Section of Cell Biology and Biophysics, University of Athens, Panepistimiopolis, Kouponia 157 01, Athens, Greece. E-mail: shamodr@atlas.uoa.gr

(Received 10 November 1995; accepted 23 December 1996)

Abstract

The sugar moiety of the title compound, $\text{C}_{12}\text{H}_{15}\text{NO}_8 \cdot \text{C}_2\text{H}_6\text{O}$, has a ${}^4\text{C}_1$ conformation. The nitrophenyl group adopts a planar conformation. The glycosidic linkage is α . The angle between the 'best planes' through the saccharide and aglycon residues is $71.5(1)^\circ$.

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 α -D-mannopyranoside (α -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.