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Synthesis and Characterization of the Monomeric Three-Coordinate Indium Thiolate and Selenolate Complexes $In[E(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_3$ (E = S, Se)

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The synthesis and characterization of the monomeric neutral three-coordinate indium thiolate and selenolate derivatives $In[S(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_3$ (**1**) and $In[Se(2,4,6\text{-}t\text{-}Bu_3C_6H_2)]_3\cdot 2PhMe$ (**2**) are described. Compound **1** was synthesized by the reaction of $In[N(SiMe_3)_2]_3$ with 3 equiv of $HS(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ in toluene whereas **2** was obtained by the reaction of $InEt_3$ with 3 equiv of $HSe(2,4,6\text{-}t\text{-}Bu_3C_6H_2)$ in the same solvent. The compounds display an essentially planar trigonal coordination at the indium atom with an average In–S bond length of 2.398(6) Å and an average In–Se distance of 2.505(3) Å. The compounds were characterized by IR and ^{1}H NMR (^{77}Se NMR in the case of **2**) spectroscopy and by X-ray crystallography. Crystal data with Mo Kα (λ = 0.710 69 Å) at 130 K: **1**, a = 10.244(3) Å, b = 26.31(2) Å, c = 20.070(10) Å, β = 90.74°, V = 5409(5) Å^3, Z = 4, space group $P2_1/n$, 4834 ($I > 2.5\sigma(I)$) data, R = 0.061; **2**, a = 14.538(4) Å, b = 14.796(3) Å, c = 16.701(5) Å, α = 85.65(2)°, β = 83.60(2)°, γ = 61.64(2)°, V = 3140.4(13) Å^3, Z = 2, space group $P\bar{1}$, 8415 ($I > 3\sigma(I)$) data, R = 0.049.

Introduction

The number of well-characterized molecular compounds that have bonds between the heavier main group 3 and 6 elements is relatively small. This is surprising owing to the technological importance of their binary derivatives which can have useful electronic and optoelectronic properties.[1–3] In the case of indium only a handful of compounds involving the In–S or In–Se moiety have, in fact, been structurally characterized. These include the molecular and polymeric compounds $[I_2InSEt]_n$,[4] $[Et_2O\cdot In\{S(2,4,6\text{-}(CF_3)_3C_6H_2)\}_3]$,[5] $[PPh_4][BrIn(SPh)_3]$,[6] $[NEt_4][XIn(SPh)_3]$ (X = Cl, Br, I),[6] $K_8[In_4S_{10}]\cdot 16H_2O$,[7] $[I_2InSeEt]_n$,[4] $[Et_3SiSeInSe]_n$,[8] $[(Me_3CCH_2)_2InSePh]_2$,[9] $[In(SePh)_3]_n$,[10] $[In(SePh)_3(py)_2]$,[10] $K_8[In_4Se_{10}]\cdot 16H_2O$,[9] $[PPh_4]_4[In_2Se_{21}]$,[11] $[\{Cp(Co)_3Mo\}_4In_4S_4]$,[12] $[\{Cp(Co)_2Fe\}_4In_4Se_4]$,[12] and $[Cu_6In_3(SEt)_{16}]^-$ [13] and the binary species In_nS_m and In_nSe_m.[14] A common feature of all these compounds is that they display a coordination number of at least 4 at indium. The formation of species with lower metal coordination numbers requires the use of very bulky ligands to prevent association. Previous work has led to the isolation of compounds of the formula $M(EMes^*)_3$ (M = Al, E = S; M = Ga; E = S, Se; Mes* = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$)[15,16] and has shown that the $-EMes^*$ (E = S, Se) ligand[16,17] is suitable for the stabilization of lower coordination in the case of aluminum and gallium. The synthesis and characterization of the corresponding indium derivatives are now described.

Experimental Section

General Procedures. All reactions were performed under N_2 by using either modified Schlenk techniques or a Vacuum Atmospheres HE 43-2 drybox. Solvents were freshly distilled from a sodium potassium alloy and degassed three times before use. Commercially available $InCl_3$ (Cerac), n-BuLi (1.6 M solution in hexane), C_2H_5Br (Kodak), and $HN(SiMe_3)_2$ (Aldrich) were used as received; $In[N(SiMe_3)_2]_3$,[18] HSMes*,[19] $InEt_3$,[20] and HSeMes* [20,21] were prepared by published procedures. Infrared spectra were recorded in the range of 4000–200 cm^{-1} as a Nujol mulls between CsI plates using a Perkin-Elmer PE 1430 spectrometer. ^{1}H NMR and ^{77}Se NMR spectra were recorded in C_6D_6 solutions on a General Electric QE 300 spectrometer (300 and 57.30 MHz) by using C_6D_6 and $(PhSe)_2$ as standards.

In(SMes*)$_3$ (1). $In[N(SiMe_3)_2]_3$ (0.62 g, 1.04 mmol) was dissolved in toluene (20 mL), and a solution of 0.869 g of HSMes* (3.12 mmol) in toluene (20 mL) was added slowly via a double-tipped needle. During the addition, the colorless solution became pale yellow. It was stirred for 18 h at room temperature and filtered, whereupon the volume was reduced to *ca.* 10 mL. Storage in a −20 °C freezer overnight resulted in the growth of pale yellow crystals that were suitable for X-ray diffraction studies. Yield: 0.88 g, 89%. Mp: 236–237 °C. IR: ν(C–S) = 642 cm^{-1}, ν(In–S) = 365 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.48 (s, 2H, m-H), 1.57 (s, 18H, o-t-Bu), 1.34 (s, 9H, p-t-Bu).

In(SeMes*)$_3$·2PhMe (2). $InEt_3$ (0.27 g, 1.33 mmol) was dissolved in toluene (10 mL), and a solution of freshly prepared HSeMes* (1.3 g, 4 mmol) in toluene (30 mL) was added dropwise. The reaction commenced immediately. The formation of gas bubbles (ethane) was readily apparent. After 30 min of stirring at room temperature, the pale yellow solution became cloudy. The mixture was stirred for another 18 h, during which time it turned clear. Upon reduction of the volume to *ca.* 20 mL and storage of the solution in a −20 °C freezer, yellow crystals of **2** were obtained. When the crystals were dried under reduced (0.1 mm) pressure, they became a yellow powder which contained no toluene. Yield: 1.25 g, 78%. Mp: dec >200 °C (turns orange, melts at 247–249 °C,

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Table I. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{54}H_{87}InS_3$	$C_{68}H_{103}InSe_3$
fw	947.2	1228.1
crystal description	colorless plates	pale yellow parallelepipeds
crystal size, mm	0.34 × 0.32 × 0.12	0.5 × 0.625 × 0.95
a, Å	10.244(3)	14.538(4)
b, Å	26.31(2)	14.796(3)
c, Å	20.070(10)	16.701(5)
α, deg		85.65(2)
β, deg	90.74(3)	83.60(1)
γ, deg		61.64(2)
V, Å^3	5409(5)	3140.4(13)
Z	4	2
space group	$P2_1/n$	$P\bar{1}$
d(calc), g/cm^3	1.163	1.299
lin abs coeff, cm^{-1}	5.84	21.51
2θ range, deg	0–50	0–55
pbs/ref	4834 ($I > 2.5\sigma(I)$)	8415 ($I > 3\sigma(I)$)
no. of variables	523	583
R, R_w	0.061, 0.067	0.049, 0.052

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Selected Atoms of **1** and **2**

atom	x	y	z	U_{iso}
		In(SMes*)$_3$		
In(1)	1291(1)	2098(1)	1539(1)	18(1)
S(1)	540(3)	2593(1)	613(1)	25(1)
S(2)	1878(2)	2529(1)	2555(1)	24(1)
S(3)	1124(2)	1195(1)	1383(1)	22(1)
C(1)	639(8)	2091(3)	0(4)	18(2)
C(19)	2811(8)	3038(3)	2186(4)	19(3)
C(37)	1966(8)	973(3)	2124(4)	17(3)
		In(SeMes*)$_3$		
In(1)	3249(1)	2676(1)	2473(1)	20(1)
Se(1)	5081(1)	1918(1)	2892(1)	23(1)
Se(2)	1716(1)	3435(1)	3510(1)	27(1)
Se(3)	2871(1)	2603(1)	1062(1)	25(1)
C(1)	5692(4)	1866(4)	1768(3)	21(2)
C(19)	2592(4)	3340(4)	4357(3)	21(2)
C(37)	1382(4)	3558(4)	1323(3)	19(2)

Table III. Important Bond Distances (Å) and Angles (deg) and Other Structural Parameters for **1** and **2** (E = S, Se)

	In(SMes*)$_3$	In(SeMes*)$_3$·2PhMe
M–E(1)	2.389(3)	2.510(1)
M–E(2)	2.403(3)	2.506(1)
M–E(3)	2.401(3)	2.501(1)
E(1)–C(1)	1.806(9)	1.976(5)
E(2)–C(19)	1.811(9)	1.960(6)
E(3)–C(37)	1.806(9)	1.962(5)
E(1)–In–E(2)	118.5(1)	119.8(1)
E(1)–In–E(3)	114.6(1)	122.6(1)
E(2)–In–E(3)	126.4(1)	117.5(1)
In–E(1)–C(1)	96.4(3)	92.7(2)
In–E(2)–C(19)	97.5(3)	93.3(1)
In–E(3)–C(37)	100.4(3)	90.4(2)
dist of In from E(1)–E(2)–E(3) plane	0.092	0.054
shortest In–H dist	2.590 (In···H52c)	2.900 (In···H35a)

presumably formation of (Mes*Se)$_2$). IR: ν(C–Se) = 458 cm^{-1}, ν(In–Se) = 253 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.52 (s, 2H, *m*-H), 1.67 (s, 18H, *o*-*t*-Bu), 1.403 (s, 9H, *p*-*t*-Bu). ^{77}Se NMR (C_6D_6): δ 255.9 (s).

X-ray Crystallographic Studies. The data for **1** and **2** were collected at 130 K with a Syntex P2$_1$ diffractometer by using graphite-monochromated Mo Kα radiation. The diffractometer was equipped with a locally modified LT-2 low-temperature device. Calculations were carried out with the SHELXTL-Plus program system[22] installed on a MicroVax 3200. In both cases, scattering factors were from common sources[23] and an absorption correction was applied using the method described in ref 24. X-ray quality-crystals were grown from toluene. The crystals were removed from the Schlenk tube under a stream of N_2 and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and immediately placed in the low-temperature nitrogen stream as described in ref 25. Some details of the data collection and the refinements are given in Table I. Further details are provided in the supplementary material. The structure of **1** was solved by using of the coordinates of Al(SMes*)$_3$;[15] the structure of **2** was solved by using the coordinates of Ga(SeMes*)$_3$·2PhMe.[16] They were refined by full-matrix least-squares procedures. In both cases, hydrogen atoms were included by the use of a riding model with C–H distances of 0.96 Å and fixed isotropic thermal parameters of 0.03 Å^2 for **1** and 0.04 Å^2 for **2**. All non-hydrogen atoms, except those of the solvent molecules in **2**, were refined with anisotropic thermal parameters. One of the toluene molecules in **2** was found to be disordered and could not be modeled satisfactorily. Fractional coordinates and isotropic thermal parameters for selected atoms are given in Table II; important bond distances and angles for **1**, **2**, and related species are provided in Tables III and IV.

Results

Syntheses. In(SMes*)$_3$ (**1**) was prepared by the reaction of In[N(SiMe$_3$)$_2$]$_3$ with 3 equiv of HSMes* in toluene according to eq 1. Attempts to prepare In(SeMes*)$_3$ via a similar route were

$$\mathrm{In[N(SiMe_3)_2]_3 + 3HSMes^* \rightarrow In(SMes^*)_3 + 3HN(SiMe_3)_2} \quad (1)$$

unsuccessful. For example, heating the mixture in refluxing toluene for several hours resulted in the recovery of unreacted In[N(SiMe$_3$)$_2$]$_3$. Similarly, attempts to synthesize **2** by the reaction InCl$_3$ and LiSeMes* in toluene did not afford the desired product owing, most probably, to the low solubility of InCl$_3$ in toluene. Instead, In(SeMes*$_3$)·2PhMe (**2**) was prepared in good yield by the reaction of InEt$_3$ with 3 equiv of freshly reduced HSeMes* in toluene, as shown in eq 2.

$$\mathrm{InEt_3 + 3HSeMes^*} \xrightarrow{\text{toluene}} \mathrm{In(SeMes^*)_3{\cdot}2PhMe + 3C_2H_6} \quad (2)$$

Structural Descriptions. The structure of the molecule In(SMes*)$_3$ (**1**) is illustrated in Figure 1. It consists of well-separated, monomeric, neutral molecules with no crystallographically imposed symmetry. The indium atom is surrounded in a distorted trigonal planar fashion by three thiolate groups with In–S bond lengths in the narrow range 2.389(3)–2.403(3) Å. Significant deviations (up to 6.4°) from idealized 120° angles at indium were observed. The average S–C distance is 1.81(2) Å, and the average In–S–C angle is 98.1(1)°. The aromatic rings of the [SMes*]$^-$ ligands form an irregular propeller-like arrangement around the S$_3$ plane with angles of 72.4, 87.6, and 88.2° between each ring and the plane described by the three sulfurs. The ipso carbons are located 0.49, 1.17, and 0.32 Å above the InS$_3$ array, such that angles of 15.6, 40.3, and 10.0° are formed between this plane and the S–C vectors. The angles between the aromatic ring planes and the S–C(ipso) vectors are 7.88° for S(1) and 13.0° for S(3), where the rings attached to S(1) and S(3) are inclined toward the metal. The angle at S(2) is 13.3°, but the corresponding phenyl ring is bent away from the metal. The shortest In···H approaches are 2.590 Å (H52c) and 2.903 Å (H19c). There are no significant distortions apparent in the corresponding *t*-Bu groups.

The X-ray structure of **2** consists of well-separated, monomeric, neutral units with an essentially trigonal planar environment at

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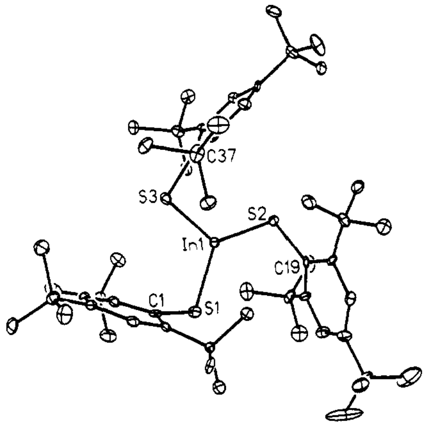

Figure 1. Computer-generated plot of **1** (thermal ellipsoids show 30% occupancy). H atoms are omitted for clarity.

Table IV. Comparison of Selected Bond Distances (Å) and Angles (deg) of **1** and **2** with Those of M(SMes*)$_3$ (M = Al, Ga) and M(SeMes*)$_3$

	Al	Ga	In
M–S	2.177(2)	2.197(2)	2.389(3)
	2.191(2)	2.207(1)	2.403(3)
	2.187(2)	2.212(1)	2.401(3)
S–M–S	115.1(1)	115.6(1)	114.6(1)
	118.4(1)	118.5(1)	118.5(1)
	125.9(1)	125.5(1)	126.4(1)
M–S–C	98.7(1)	99.1(1)	96.4(3)
	103.0(1)	102.6(1)	100.4(3)
	99.4(1)	99.4(1)	97.5(3)
MS$_3$/Mes*	70.5	72.3	72.4
	87.4	85.5	87.6
	89.6	88.3	88.2
MS$_3$/SC	8.5	10.6	10.0
	14.0	13.6	15.6
	39.7	37.3	40.3
M–Se		2.326(1)	2.501(1)
		2.322(1)	2.506(1)
		2.324(1)	2.510(1)
Se–M–Se		117.7(1)	117.5(1)
		119.7(1)	119.8(1)
		122.5(1)	122.6(1)
M–Se–C		94.1(2)	92.7(2)
		95.3(2)	93.3(1)
		92.3(2)	90.4(2)
MSe$_3$/Mes$_3$*		83.2	84.1
		84.2	85.6
		87.7	87.3
MSe$_3$/SeC		4.9	6.7
		12.0	12.2
		13.9	15.2

indium. There are also two noninteractive toluene molecules in each unit cell. The three –SeMes* groups surround the indium atom in a propeller-like fashion. The molecular structure is given in Figure 2, and important bond lengths and angles are provided in Table III. The almost trigonal planar InSe$_3$ core has In–Se bond lengths whose average is 2.505(3) Å. The Se–In–Se angles range from 117.5(1) to 122.6(1)°, and the sum of the angles at indium is 359.9°. The indium atom is located 0.054 Å above the Se$_3$ plane. The average Se–C distance is 1.97(1) Å, and the angles between the Se$_3$ planes and the aromatic rings are 95.9, 94.6, and 92.7°, respectively. The ipso carbons are located 0.53, 0.23, and 0.41 Å above the plane of the three selenium atoms. The angles between the Se–C bond and the Se$_3$ plane are 15.5, 6.7, and 12.2°. In addition, there are angles of 17.1° (Se(1)) and 15.7° (Se(2)) between the Se–C bond and the plane of the aromatic rings, with the result that the rings are inclined toward the metal; the angle at Se(3) is 17.0°, the attached ring bending away from the metal. The shortest In···H approaches are 2.90 Å (H35a) and 2.93 Å (H10a); there is no agostic interaction present.

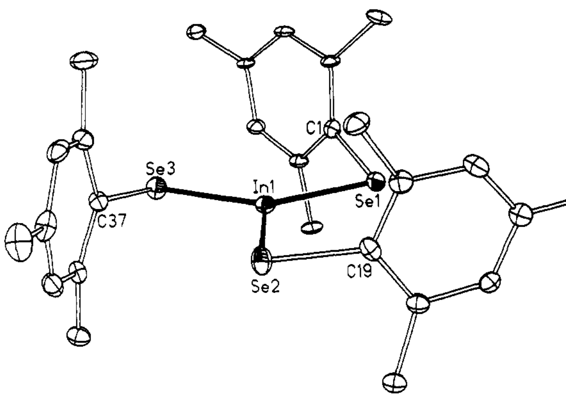

Figure 2. Computer-generated plot of **2**. H atoms and CH$_3$ groups on the *t*-Bu substituents are omitted for clarity.

Discussion

Compounds **1** and **2** were synthesized by different types of exchange reactions. The synthesis of **1** involved the treatment of In[N(SiMe$_3$)$_2$]$_3$ with 3 equiv of the thiol HSMes* whereas in the synthesis of **2** InEt$_3$ was employed as the indium substrate. These precursors were chosen because of their solubility in noncoordinating hydrocarbon solvents. More conventional routes to indium thiolates involving treatment of InCl$_3$ with an alkali metal thiolate salt in a coordinating solvent have led to products such as [Et$_2$O·In{S(2,4,6-(CF$_3$)$_3$C$_6$H$_2$)}$_3$],[5] in which the donor molecule is strongly bound to indium.

The X-ray crystal structures of **1** and **2** are rare instances of molecules in which indium has been shown to be three-coordinate. Prior examples include In[CH(SiMe$_3$)]$_3$,[26] In[P(*t*-Bu)$_2$]$_3$,[27] In$_2$R$_4$ (R = –CH(SiMe$_3$)$_2$),[28] and InMes$_3$.[29] Structurally characterized species that have In–S or In–Se bonds invariably have indium in a coordination number of 4 or greater. As a result of the lower coordination number at the metal, **1** and **2** display the shortest In–S (2.398(6) Å (average) and In–Se (2.506(3) Å (average)) bonds that have been reported to date (*cf.* In–S = 2.418(5) (average) in [Et$_2$O·In{S(2,4,6-(CF$_3$)$_3$C$_6$H$_2$)}$_3$] and 2.417 and 2.539 Å for the terminal In–S and In–Se bonds in [In$_4$E$_{10}$]$^{8-}$ (E = S, Se)).[7] The structure of **2** may also be contrasted with that of the less-hindered species [In(SePh)$_3$]$_n$,[10] which has a polymeric structure in which six-coordinate indiums are linked by μ_2-bridging –SePh groups. In this species the In–Se bonds average 2.776(8) Å in length.

A comparison of the structure of **1** with its previously published aluminum and gallium analogues (Table IV) reveals a very close correspondence of structural detail. The three compounds have very similar patterns of distortion of the angles at the metal. In addition, the M–S–C angles at the sulfurs are very similar although there is some evidence of narrower angles in the indium species. This suggests that there is some steric crowding and consequent strain in the aluminum and gallium species that have been relieved in the indium analogue owing to the longer In–S bonds. The indium–sulfur bonds are notably longer (*ca.* 0.2 Å) than those observed in the aluminum or gallium analogues. The rather large difference in length between the Ga–S and In–S distances (the corresponding difference between Al–S and Ga–S distances is only 0.02 Å) is due mainly to the small relative size and lower electropositive character of gallium owing to the first filling of a d shell. A comparison of the data for **2** and Ga(SeMes*)$_3$ reveals a very similar pattern. The In–Se bond lengths are almost 0.2 Å longer than those of Ga–Se. There are also similarities

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in the distortions of the angles at gallium and indium. In addition, the In–Se–C angles are marginally narrower than those observed in the gallium species.

Other structural features worthy of mention are the angles between the ME_3 (E = S, Se) plane and the planes of the Mes* rings and also the angles between the S–C or Se–C vectors and the ME_3 (E = S, Se) plane (Table IV). The data appear to indicate that in these molecules steric interference in the more crowded species $Al(SMes^*)_3$ and $Ga(SMes^*)_3$ is reduced by twisting an SMes* group out of the MS_3 plane by rotation around the M–S bond rather than by opening the M–S–C angles. This suggests that π-bonding, if it is present, is rather weak or, at least, is worth less in terms of energy compared to distortions such as changing the M–S–C or S–C/Mes* plane angles. It should be borne in mind, however, that the π-interactions in such compounds are divided over three M–E bonds and are thus weaker and more difficult to detect. Species in which there is a 1:1 ratio of M:E such as R_2MER' offer a better chance for the detection of M–E interactions, and indeed a recent investigation of the compound $\{(Me_3Si)_2CH\}_2GaTeSi(SiMe_3)_3$[30] has shown that there is a rotation barrier of a *ca.* 50 kJ mol^{-1} around the Ga–Te bond. Although there is not structural proof for such bonding in **1** or **2**, it is possible that there might be a weak In–S or In–Se π-interaction in these species. Variable-temperature ^1H NMR studies of **1** and **2** display no evidence of dynamic behavior.

The IR spectrum of **1** reveals a band at 365 cm^{-1} that could be assigned to an In–S stretching mode. This frequency is slightly higher than bands observed for $K_8In_4S_{10}\cdot16H_2O$,[8] which has four-coordinate indium and longer In–S bonds. A similar result was found by comparison of the stretching frequencies of the $M(EMes^*)_3$ (M = Al, Ga) compounds with those of other known compounds displaying higher coordination numbers.[13,14] The In–Se stretching frequency for **2** may be assigned at 253 cm^{-1}, which is slightly different from that for the polymeric $[I_2InSeEt]_n$, which was observed at 290 cm^{-1}.[4] However, the number of data available to compare these values is very limited and further data and compounds will be required to make definitive assignments.

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Supplementary Material Available: Full tables of crystallographic data, atom coordinates, bond distances and angles, hydrogen coordinates and thermal parameters (23 pages). Ordering information is given on any current masthead page.

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[30] Uhl, W.; Layh, M.; Becker, G.; Klinkhammer, K. W.; Hildenbrand, T. *Chem. Ber.* **1992**, *125*, 1547.