THE PROPERTIES AND STRUCTURES OF TRIS(BENZENETHIOLATO)INDIUM(III)-BIS-PYRIDINE ADDUCT, AND OF TRIS(BENZENESELENOLATO)INDIUM(III)

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Abstract—The bis-pyridine adduct of $In(SC_6H_5)_3$ has been prepared. A crystal structure determination shows that the molecule has two different conformations in the solid state, related to the orientations of the phenyl rings of the SC_6H_5 ligand. The crystalline form of $In(SeC_6H_5)_3$ is a homopolymer in which six-coordinate indium atoms are linked through bridging selenium atoms. The phenyl groups of the SeC_6H_5 ligand show an interesting disorder pattern. The structure of $In(SC_6H_5)_3$ is discussed in this context.

Recent papers¹⁻³ from this laboratory have described three different preparative routes to tris (benzenethiolato)indium(III). The compound is apparently a homopolymer, whose structure can be broken down by neutral or anionic donor ligands to give the appropriate mononuclear adducts; an X-ray crystallographic study of the tetraphenylphosphonium salt of $[InBr(SPh)_3]^-$ has also been reported.¹ The selenium analogue has similar properties, extending to its behaviour as a Lewis acid.²

We have now been able to obtain $In(SeC_6H_5)_3$ in crystalline form, and to show that this compound has a homopolymeric structure in the solid state. It has not been possible to carry out similar studies with $In(SC_6H_5)_3$, but the neutral adduct $In(SC_6H_5)_3py_2$ (py = pyridine) has been investigated, and the X-ray results confirm previous arguments based on spectroscopic studies.¹ The results are compared with those for other indium(III) compounds, and with certain other selenolato derivatives of d^{10} metal ions.

EXPERIMENTAL

Preparative

(i) Tris(benzenethiolato)indium(III)-bis-pyridine. Tris(benzenethiolato)indium(III) was prepared by the reaction of indium metal with diphenyldisulphide in refluxing toluene.² In(SC₆H₅)₃ (1 g) was dissolved in warm pyridine (5 cm³), and the resultant solution allowed to evaporate slowly at room temperature. The crystals obtained after *ca* 2 months were collected and dried. The IR and ¹H NMR spectra confirmed the presence of both pyridine and SC₆H₅ ligand (Found : C, 55.7; H, 4.23. Calc. for C₂₈H₂₅N₂S₃In : C, 56.0; H, 4.20%).

(ii) Tris(benzeneselenolato)indium(III). $In(SeC_6H_5)_3$ was prepared by the reaction of indium metal with diphenyldiselenide in refluxing toluene.² Crystals suitable for X-ray crystallography were obtained by the slow evaporation of a dilute

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solution in toluene $(0.1 \text{ g in } 100 \text{ cm}^3)$ under a slow stream of nitrogen over a period of 10 days.

Structure determinations

Suitable crystals of either $In(SC_6H_5)_3py_2$ (1) or $In(SeC_6H_5)_3$ (2) were sealed in thin-walled glass capillaries and mounted and aligned on a Syntex P21 automated diffractometer. Data collection followed the procedures described previously.⁴ The intensities of three monitor reflections were measured after every 100 reflections, and did not change significantly during data collection. The intensities were corrected for Lorentz and polarization effects. No absorption corrections were used in the refinement of 1, because of the low absorption coefficient; in 2, subsequent accidental loss of the crystal prevented the application of an absorption correction, but in the event this appears to have had little effect (see below). Details of cell constants and other relevant experimental data are given in Table 1.

For 1, there were no systematic absences, and the space group $P\overline{1}$ was used in the refinement, and taken to be correct in view of the successful refinement. The position of the indium atoms was found by direct methods, and the structure was refined by block matrix methods, using the program SHELX.⁶ At this point, two different forms of the molecule were identified, and both indium atoms [In(1), In(2)] were included in each block; in addition, block 1 contained six sulphur atoms, four nitrogen and 16 carbon atoms [C(11)—C(34)] and a scale factor (173)

parameters), and block 2 contained In(1), In(2), 40 carbon atoms [C(35)—C(90)] and a scale factor (179 parameters). Indium, sulphur and nitrogen atoms were refined anisotropically, and carbon atoms isotropically. Hydrogen atoms were subsequently included in ideal positions [r(C-H) = 0.95 Å], and assigned U-values $1.10 \times$ those of the carbon atoms attached to the hydrogen in question. The function minimized during the least-squares refinement was $(|F_o| - |F_c|)^2$, and a weighting scheme $1/[\sigma^2(F) + pF^2]$ was employed (p = 0.00001). The small residual electron density in the final difference map was not at any chemically significant position, and there was not secondary extinction.

For 2, the systematic absences (*hkl*, h+k =2n+1; h0l, l = 2n+1) indicated the space group C2/c or Cc, but the systematic weakness suggested C2/c. Eventual structural solution and refinement in C2/c, together with a failure to obtain significantly improved results in Cc, confirmed the former as being the correct space group. The structure was solved by direct methods, using MULTAN 78. The indium atom was constrained to lie on an inversion centre, and Se(1) on a two-fold axis (see Fig. 1). When anisotropic refinement of In and Se atoms converged, the presence of large thermal ellipsoids for the carbon atoms, plus the fact that the asymmetric unit contains one and one half phenyl rings as indicated by the elemental analyses, suggested disorder in the phenyl rings. The phenyl group bonded to Se(1) requires two-fold symmetry within the ring, but is disordered about the two-fold axis

	1	2
Formula, <i>fw</i>	$C_{28}H_{25}N_2S_3In, 600.4$	$C_{18}H_{15}Se_{3}In, 582.7$
Cell constants at 22°C	$a, 9.552(2)$ Å; $\alpha, 91.92(3)^{\circ}$	a, 12.565(5) Å
	b, 15.314(5) Å; β, 93.58(2)°	b, 20.095(14) Å; β, 112.58(3)°
	c, 19.370(6) Å; γ, 106.12(2)°	c, 7.250(3) Å
Cell volume (Å ³)	2713(1)	1690(2)
Space group	ΡĪ	C2/c
Ζ	4	4
d (calc.), d (exp.) (g cm ⁻³)	1.47, 1.45	2.29, 2.25
Absorption coefficient (cm ⁻¹)	10.21	31.86
Radiation	$Mo-K_{\alpha} (\lambda = 0.71069 \text{ Å})$	Mo- K_{α} ($\lambda = 0.71069$ Å)
2θ (max) for data collection	45°	50°
Scan width	$K_{\alpha_1} - 0.8^{\circ}$ to $K_{\alpha_2} + 0.8^{\circ}$	$K_{\pi_1} - 0.8^\circ$ to $K_{\pi_2} + 0.8^\circ$
Total reflections measured	$5397(+h, \pm k, \pm l)$	$1762(+h, +k, \pm l)$
Unique "observed" reflections $[I \ge 3\sigma(I)]$	4275	706
$R = (\Sigma F_{\rm o} - F_{\rm c}) / \Sigma F_{\rm o})$	0.0457	0.0605
$R_{\rm w} = (\Sigma_{\rm w} (F_{\rm o} - F_{\rm c})^2 / (\Sigma_{\rm w} F_{\rm o} ^2)^{1/2}$	0.0568	0.0675
Shift/esd (max) in the final cycle	0.04	0.02
Max (eA^{-3}) in the final dimap	0.91	1.6

Table 1. Summary of crystal data, intensity collection and structural refinement for 1 and 2



Fig. 1. ORTEP diagram showing a chain of $In(SeC_6H_5)_3$ parallel to the *a* axis. The Se and In atoms are drawn with 50% probability ellipsoids; and C atoms are arbitrarily small, and have 50% occupancy. Hydrogen atoms have been omitted for the sake of clarity. For symmetry related positions, see footnotes to Table 2.

passing through Se(1), and this axis generates the carbon atoms of ring 1B from those of 1A, with all of the carbon sites having 50% occupancy. The ring bonded to Se(2), which is the selenium atom on the general position, is also disordered, and was therefore divided into two sets "2A" and "2B", with each set having 50% occupancy. The carbon atoms were refined isotropically, and no attempt was made to include hydrogen atoms. The function minimized during full-matrix least-squares refinement was $w(|F_0| - |F_c|)^2$ and in the final cycles, a weighting scheme of the form $w = 1/[\sigma^2(F) + 0.00001F^2]$ was employed. No evidence of secondary extinction was noticed. A final difference Fourier map contained a few peaks of the order of $1-1.5 \text{ e}^{\text{Å}-3}$ in the vicinity of the indium and selenium atoms, which may be due to uncorrected absorption effects (see above).

Selected bond distances and angles for 1 and 2 are given in Tables 2 and 3, respectively, and Figs 1-3 show the molecular structures with the atomic numbering schemes. Tables of atomic coordinates, anisotropic thermal parameters, and observed and calculated structure factors for each compound are available as supplementary material from the Editor.



Fig. 2. ORTEP diagram of form A of $In(SC_6H_5)_3py_2$, showing the atomic numbering scheme. Atoms identified by numbers are carbons.

RESULTS AND DISCUSSION

The structure of $In(SC_6H_5)_3py_2$

The results of the X-ray crystallographic studies show that the bis-pyridine adduct of $In(SC_6H_5)_3$ is

In(1)—S(1)	2.448(3)	S(1) - In(1) - S(2)	111.5(1)
In(1)—S(2)	2.472(3)	S(1)—In(1)—S(3)	119.9(1)
In(1)—S(3)	2.455(3)	S(2)—In(1)—S(3)	128.3(1)
In(1) - N(1)	2.408(7)	S(1) - In(1) - N(1)	97.3(2)
In(1) - N(2)	2.374(8)	S(2) - In(1) - N(1)	88.6(2)
In(2)— $S(4)$	2.447(3)	S(3) - In(1) - N(1)	79.7(2)
$\ln(2)$ —S(5)	2.468(3)	S(1) - In(1) - N(2)	97.7(2)
$\ln(2) - S(6)$	2.459(3)	S(2) - In(1) - N(2)	85.7(2)
ln(2) - N(3)	2.390(6)	S(3) - In(1) - N(2)	93.0(2)
ln(2) - N(4)	2.390(7)	N(1) - ln(1) - N(2)	165.0(3)
S(1) - C(11)	1.77(1)	S(4) - In(2) - S(5)	109.4(1)
S(2) = C(21) S(2) = C(21)	1.77(1)	S(4) - In(2) - S(6)	121 (1)
S(3) = C(31) S(4) = C(41)	1.77(1)	S(3) = In(2) = S(0) S(4) = In(2) = N(3)	102 5(2)
S(4) = C(41) S(5) = C(51)	1.77(1)	S(4) = In(2) = In(3) S(5) = In(2) = N(3)	88 6(2)
S(5) - C(51)	1.77(1)	S(5) = In(2) = N(3) S(6) = In(2) = N(3)	81 3(2)
N(1) - C(71)	1.77(1) 1 33(1)	S(4) = In(2) = N(4)	94.8(2)
N(1) - C(75)	1.33(1)	S(5) - In(2) - N(4)	83 8(2)
N(2) - C(76)	1.33(1)	S(6) - In(2) - N(4)	92.1(2)
N(2) - C(80)	1.32(1)	N(3) - In(2) - N(4)	162.6(3)
N(3) - C(81)	1.32(1)	In(1) - S(1) - C(11)	100.8(3)
N(3) - C(85)	1.33(1)	In(1) - S(2) - C(21)	100.8(4)
N(4)C(86)	1.33(1)	In(1) - S(3) - C(31)	108.6(3)
N(4)-C(90)	1.32(1)	In(2) - S(4) - C(41)	108.3(3)
Ring C(11)-C(16)		In(2) - S(5) - C(51)	101 9(4)
Mean C—C	1.37(8)	In(2) - S(6) - C(61)	108.7(3)
Mean C—C—C	120(4)	In(1) - N(1) - C(71)	117.2(7)
	(')	In - N(1) - C(75)	125.3(5)
Ring C(21)-C(26)		C(71) - N(1) - C(75)	117.2(8)
Mean C-C	1.37(4)	In(1) - N(2) - C(80)	118 6(9)
Mean C-C-C	120(3)	In(2) - N(3) - C(81)	123.7(6)
Ring $C(31) - C(36)$		$I_{n}(2) - N(3) - C(85)$	117 2(6)
Mean C-C	1 36(8)	C(81) - N(3) - C(85)	117.2(0) 118 $4(7)$
Mean C-C-C	120(4)	In(2) - N(4) - C(86)	123.0(7)
$\mathbf{D}_{\mathrm{inv}}^{\mathrm{inv}} \mathcal{O}(A1) = \mathcal{O}(A6)$	120(1)	$I_{n}(2) = N(4) - C(00)$	110 0(6)
$\operatorname{King} C(41) - C(40)$	1 27(4)	III(2) - II(4) - C(90)	110.0(0)
Mean C-C-C	1.37(4)	C(80) - I(4) - C(90) S(1) - C(11) - C(12)	110.7(0)
	120(3)		119.5(9)
Ring C(51)—C(56)	1 20(4)	S(1) - C(11) - C(16)	122.7(8)
Mean CC	1.38(4)	S(2) - C(21) - C(22)	120.9(7)
Mean C-C-C	120(2)	S(2) = C(21) = C(26)	121./(8)
Ring C(61)C(66)	4	S(3)-C(31)-C(32)	118.8(7)
Mean C—C	1.38(3)	S(3)—C(31)—C(36)	120.3(9)
Mean C—C—C	120(1)	S(4) - C(41) - C(42)	119.2(8)
Ring N(1), C(71)C	C(75)	S(4)-C(41)-C(46)	120.0(8)
Mean C-C	1.36(2)	S(5)-C(51)-C(52)	120.7(8)
Mean C—C—C	120(3)	S(5)-C(51)-C(56)	120.6(6)
Ring N(2), C(76)C	2(80)	S(6)—C(61)—C(62)	117.8(6)
Mean C—C	1.36(4)	S(6)—C(61)—C(66)	122.7(7)
Mean C-C-C	120(4)		
Ring N(3), C(81)C	2(85)		
Mean C-C	1.36(2)		
Mean C—C—C	120(2)		
Ring N(4), C(86)C	2(90)		
Mean C-C	1.37(3)		
Mean C-C-C	120(3)		

"Esd's on average values are calculated with the use of the "scatter" formula:

$$\sigma = \left[\sum (d_t - \bar{d})^2 / (N - 1)\right]^{1/2},$$

where d_i is the *i*th, and d the mean, of N equal measurements.

InSe(1)	2.772(2)	Se(1)—In—Se(2)	97.9(1)
In—Se(2)	2.766(2)	Se(1 ^a)—In—Se(2)	82.1(1)
InSe(2 ^b)	2.789(2)	$Se(1)$ —In— $Se(2^{b})$	81.7(1)
Se(1)C(1A)	1.90(3)	$Se(1^{a})$ —In— $Se(2^{b})$	98.3(1)
Se(2)—C(11A)	1.94(3)	$Se(2)$ —In— $Se(2^b)$	97.8(1)
Se(2)—C(11B)	1.93(3)	$Se(2^{a})$ —In— $Se(2^{b})$	82.2(1)
Ring 1A, C(1A)C	(6A)	InSe(1)C(1A)	117.3(8)
Mean C-C	1.43(6)	In - Se(1) - C(1B)	110.9(8)
Mean CCC	120(5)	C(1A)—Se(1)— $C(1B)$	114.8(9)
Ring 2A, C(11A)(C(16A)	In—Se(2)—C(11A)	110.0(9)
Mean CC	1.40(5)	In-Se(2)-C(11B)	117.2(9)
Mean C—C—C	120(4)	C(11A)—Se(2)—C(11B)	114(1)
Ring 2B, C(11B)C	C(16B)	Se(2)C(11A)C(12A)	120(2)
Mean C-C	1.42(5)	Se(2) - C(11A) - C(16A)	123(3)
Mean CCC	120(2)	Se(2) - C(11B) - C(12B)	122(2)
In · · · In ^b	3.625	Se(2)C(11B)C(16B)	115(2)

Table 3. Bond distances (Å) and angles (deg) for $In(SeC_6H_5)_3$

1. The symmetry related positions are: a, -x, -y, -z; b, x, -y, $z-\frac{1}{2}$.

2. The carbon atoms of ring 1A are related to those of 1B by -x, y, $\frac{1}{2}-z$ and all the carbon atoms have 50% occupancy.

3. Esd's on average values have been calculated as in Table 2.



Fig. 3. ORTEP diagram of form B of In(SC₆H₅)₃py₂, showing the atomic numbering scheme. Atoms identified by numbers are carbons.

indeed a mononuclear species. The molecular structure is essentially based on a distorted trigonal bipyramidal InS_3N_2 kernel, with the sulphur atoms of the benzenethiolate ligands occupying the equatorial sites and the pyridine nitrogens in the axial positions. This compound then joins the increasingly large group of five-coordinate inorganic and organometallic compounds of indium(III), and this coordination state, which includes both trigonal bipyramidal and square-based pyramidal, must now be regarded as of equal importance with the longer established tetrahedral and octahedral stereochemistries.^{6,7}

The structure consists of two independent molecules 1A and 1B which differ in the arrangement of the phenyl rings of the ---SC₆H₅ ligands. In molecule 1A (Fig. 2), these three phenyl groups are in a cyclic arrangement, with ring C(11)—C(16)approximately normal to the other two. The dihedral angle between the plane of this ring and that of ring C(21)—C(26) is 90.3(2)°, and that C(11)-C(16) and C(31)-C(36) is between The planes of C(21)—C(26) and 84.4(2)°. C(31)—C(36) are then almost parallel, with a dihedral angle of 9.9(2)°. In 1B, the ring C(41)—C(46) is again almost normal to the other two phenyl rings, with dihedral angles of 98.9(2)° to C(51)-C(56), and 95.7(2)° to C(61)-C(66) and the latter two are at a dihedral angle of $8.2(2)^{\circ}$. Another way of describing the difference between 1A and 1B is in terms of the torsion angles involved at the In-S-C₆H₅ sites; in 1A, the angle In(1)-S(1)-C(11)-C(12) is 107.0(2)°, whereas in 1B the corresponding In(2)—S(4)—C(41)—C(46)angle is 67.2(2)°, and similarly, we find In(1) - S(1) - C(11) - C(16)at $-75.0(2)^{\circ}$, and In(2) - S(4) - C(41) - C(42) at $-117.8(2)^{\circ}$, а difference of about 40°.

Despite these significant differences in the orientation of the phenyl groups, the InS_3N_2 kernels of the two molecules are essentially identical, as are the $-SC_6H_5$ ligands in terms of their internal geometries. The N-In-N angle in 1A is 165.0(3)°, and in 1B, 162.6(3)°, both significantly less than the

180° required for trigonal bipyramidal stereochemistry. Although the S-In-S angles in 1A range from 111.5(1) to 128.3(1)°, the average is $120(3)^{\circ}$, while in 1B the average of $120(4)^{\circ}$ arises from a range of $109.4(1)-131.6(1)^\circ$. Despite the two different orientations, the average In-S bond distance is the same in both structures, namely 2.458(8) Å, very close to the average value¹ of 2.450(4) Å in the anion $[BrIn(SC_6H_5)_3]^-$. A brief review of other In—S bond lengths has been given elsewhere,¹ with distances > 2.59 Å being reported, but differences in coordination number and ligand type between the various molecules studied prevent any detailed analysis at this point. The average S-C distance in the ligand is 1.77(1) Å, with all ligands being identical within experimental error in this respect, and this value is close to that of 1.75(2) Å in the structure previously reported.¹

The average In—N bond distance is also identical in 1A and 1B, at 2.39(1) Å. In the molecule $Cl_2In(O_2CC_6H_5)py_2$, which also can be described as having a distorted trigonal bipyramidal structure with apical pyridine ligands,⁸ the relevant In—N bond lengths are 2.250(5) and 2.300(6) Å, and a brief discussion of the results for other indium(III) complexes involving neutral aromatic nitrogen donors lead to an average value for In—N over a small group of compounds of 2.28 Å, with a range of 2.238(3)–2.514(19) Å. In general then, the present results are in keeping with previous work, but the significant difference between In(SC₆H₅)₃py₂ and $Cl_2In(O_2CC_6H_5)py_2$ is not easily understood.

We return below to the relationship between this compound and the parent $In(SC_6H_5)_3$.

The structure of $In(SeC_6H_5)_3$

Figure 3 confirms that $In(SeC_6H_5)_3$ is indeed a homopolymeric structure in the solid state, with linear chains formed by indium and selenium atoms running parallel to the *a* axis of the unit cell. Each indium is coordinated by six selenium atoms, and each selenium bridges two indium atoms. Crystallographically, each indium is on a centre of inversion; Se(1) lies on a two-fold axis and Se(2) on a general position, so that In and Se(2^{a,b}) form a planar chain, with Se(1) lying alternately above and below this plane. The four atoms In, In^b, Se(1) and Se(1^a) also define a plane, perpendicular to the *b* axis, and this plane is at an angle of 89.7(1)° to a third plane involving In, Se(2), Se(2^b), Se(2^a) and Se(2^c).

The geometry of the $InSe_6$ kernel is a highly distorted octahedral, with Se—In—Se angles which vary between 81.7(1)– $98.3(1)^\circ$, with an average of 90° which is imposed by the symmetry relationships. The average In—Se bond length is 2.776(8) Å, and this appears to be the first such distance to be reported in a complex of this type. The In—Se distances in the adamantane-like $In_4Se_{10}^8$ anion⁹ are 2.543(2) for In—Se_t, and 2.565(2) Å for In—Se_{br}, but obviously the presence of the pendant phenyl groups must have some effect on the bond length in the present structure. The average In \cdots In separation is 3.625 Å, much larger than the known In—In bonding distance¹⁰ of 2.775(2) Å.

The geometry about each selenium atom is pyramidal, but the important feature of the ligand arrangement is that the phenyl rings are disorded, with each ring shown in Fig. 1 having an occupancy of 50%. The average Se—C distance is 1.92(3) Å, similar to that in $[Pb(SeC_6H_5)_3]^-$ [average value 1.91(1) Å],¹¹ (C₆H₅)₂Se₂ [1.93(5) Å]¹² and (C₆F₅)₂Se₂ [1.910(15) Å].¹² Leaving aside the polymeric structure of **2**, the M—SeC₆H₅ geometry is quite similar to that in $[Pb(SeC_6H_5)_3]^-$.

Relationship between structure and properties

The most satisfying conclusion is that the structure of $In(SeC_6H_5)_3$ is indeed the homopolymer predicted from the chemical properties of the compound, although the details of the cross-linking could not be deduced from the general insolubility of the compound in non-donor solvents, or from its reaction with neutral or anionic donors.² Crosslinking by $M \leftarrow S(Se)$ donation has frequently been proposed for the solid state structure of metal thiolates and selenolates, and the present work is in keeping with studies of $[Hg(SeCH_3)_2]_n$ and related compounds.¹³

Despite repeated attempts involving a variety of solution and vaporization techniques, we were unable to produce crystals of $In(SC_6H_5)_3$, and it is interesting to consider the possible reasons, given the relative ease with which the selenium analogue yielded good crystals. It seems certain that In-S bonds are thermodynamically stronger than In-Se bonds, which means that a homopolymeric $In(SC_6H_5)_3$ structure would be more stable to dissociation than $In(SeC_6H_5)_3$, and hence less soluble in organic solvents. In fact, the sulphur compound is soluble only in strong donors such as pyridine, or in refluxing benzene,¹ and complexation is clearly significant in the case of the donor solvents. A suitable solvent for crystallization is therefore lacking. Another factor acting against the formation of an ordered lattice may be the short In-S bonds, which as the present results show, are approx. 0.3 A shorter than In—Se, so that a regular structure such as that in Fig. 1 may be difficult to replicate for $In(SC_6H_5)_3$, since the phenyl groups of one plane

may face considerable steric hindrance in packing with those of the next layer. Thus attempts to grow crystals of $In(SC_6H_5)_3$ from the vapour phase may be vitiated by irregular growth of the homopolymer, in contrast with the regular arrangement which is obviously possible for $In(SeC_6H_5)_3$.

A final conclusion to be drawn from the structure of $In(SeC_6H_5)_3$ is that the formation of adducts, such as $In(SeC_6H_5)_3L$ (L = 2,2'-bipyridine, 1,10phenanthroline, or two triphenylphosphines) or $[InBr(SePh)_3]^-$, must involve a major rearrangement of the InSe kernel, assuming that these species are isostructural with the analogous SC_6H_5 compounds. The molecularity and stereochemistry of the species present in toluene, or in donor solvents, are clearly of importance in this context, and will be the subject of future investigations.

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