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Five-Coordination with "Hybrid" Ligands. II.[1] Nickel(II) Complexes with Polyfunctional Arsenic-Containing Ligands

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The new ligands tris(2-diphenylarsinoethyl)amine (set of donor atoms NAs_3), bis(2-diphenylarsinoethyl)amine (set NAs_2), bis(2-diphenylarsinoethyl)sulfide (set SAs_2), bis(2-diphenylarsinoethyl)oxide (set OAs_2), and the ditertiary diarsine group consisting of set As_2 1,2-bis(diphenylarsino)ethane and 1,4-bis(diphenylarsino)butane have been prepared. The coordinating ability of these ligands toward nickel salts has been investigated. Low-spin five-coordinate complexes have been obtained with the donor sets NAs_3, NAs_2, and SAs_2. Also compounds with tetrahedral, planar, and octahedral stereochemistry have been obtained. The compound $Ni[((C_6H_5)_2AsCH_2CH_2)_2NH]Br_2$ contains nickel(II) ions in both triplet and singlet ground states.

Introduction

Arsenic-containing pentacoordinate complexes are usually low spin[2-7] whereas those containing nitrogen- and oxygen-donor ligands are usually high spin.[8] As a further step in our systematic investigation into the effects of different donor atoms on the stereochemistry and spin multiplicity of complexes of the first row of transition metals, we have prepared some nickel(II) complexes with ligands containing both arsenic- and nitrogen- or oxygen-donor sites. The ligands are tris(2-diphenylarsinoethyl)amine (I, NAs_3), bis(2-diphenylarsinoethyl)amine (II, AsNAs), and bis(2-diphenylarsinoethyl)oxide (III, AsOAs). The thioether (IV, AsSAs) was also prepared. For comparison purposes, we also prepared the ω,ω'-bis(diphenylarsino)alkanes (V, AsC_nAs, $n = 2, 4$).

$N(CH_2CH_2As(C_6H_5)_2)_3$
I, NAs_3

$(C_6H_5)_2AsCH_2CH_2NHCH_2CH_2As(C_6H_5)_2$
II, AsNAs

$(C_6H_5)_2AsCH_2CH_2OCH_2CH_2As(C_6H_5)_2$
III, AsOAs

$(C_6H_5)_2AsCH_2CH_2SCH_2CH_2As(C_6H_5)_2$
IV, AsSAs

$(C_6H_5)_2As(CH_2)_nAs(C_6H_5)_2$
V, AsC_nAs

Experimental Section

Synthesis of the Ligands.—The NAs_3 was prepared as follows. $NH(CH_2CH_2Cl)_2$[9] (3.7 g, 0.015 mol) in 50 ml of previously dried tetrahydrofuran was added dropwise with continuous stirring to 20 g (0.045 mol) of $KAs(C_6H_5)_2 \cdot 2(\text{dioxane})$[10] dissolved in 200 ml of tetrahydrofuran. The solution was refluxed for 30 min and then concentrated to a small volume on a steam bath. All operations were carried out in a nitrogen atmosphere. Butanol was then added and the NaCl precipitate was filtered off. On cooling, white crystals separated which were recrystallized from butanol. *Anal.* Calcd for $C_{42}H_{42}NAs_3$: C, 64.20; H, 5.39; As, 28.61. Found: C, 64.10; H, 5.68; As, 28.50; mp 95–96°.

Analogous procedures were employed to obtain the AsOAs, AsNAs, AsSAs, and AsC_nAs ligands. The stoichiometric amounts respectively, of $NH(CH_2CH_2Br)_2$,[11] $O(CH_2CH_2Cl)_2$,[12] $S(CH_2CH_2Cl)_2$,[13] and $(CH_2)_nCl_2$ were allowed to react with 22 g (0.05 mol) of $KAs(C_6H_5)_2 \cdot 2(\text{dioxane})$.[10] The filtered solutions were concentrated under vacuum to eliminate solvent. In the case of AsSAs, AsC_2As, and AsC_4As, a crystalline product was obtained, which was recrystallized from butanol. *Anal.* Calcd for $C_{28}H_{28}As_2S$: C, 61.50; H, 5.17; As, 27.42. Found: C, 60.85; H, 5.40; As, 27.60; mp 64–65°. Calcd for $C_{26}H_{24}As_2$: C, 64.21; H, 4.89; As, 30.81. Found: C, 64.80; H, 4.90; As, 30.60; mp 114–115°. Calcd for $C_{28}H_{28}As_2$: C, 65.38; H, 5.49; As, 29.13. Found: C, 65.57; H, 5.58; As, 29.00; mp 125–127°. AsNAs and AsOAs ligands were obtained in the form of oils and used without further purification.

Preparation of the Complexes. AsNAs, AsSAs, AsOAs, and AsC_nAs Complexes.—The compounds were prepared by the following general method. A solution of 10 mmol of the diarsine ligand in 10 ml of dry butanol was added to a boiled solution of the stoichiometric amount of the appropriate nickel halide in 30 ml of butanol. The solution was concentrated until crystals were obtained. In some cases cyclohexane was added to promote precipitation. The crystals were collected using a filter funnel, washed with the solvent and petroleum ether (bp 40–70°), and dried under vacuum.

$[Ni(NAs_3)Br]B(C_6H_5)_4$.—To a solution of 10 mmol of anhydrous nickel halide dissolved in 30 ml of butanol was added 10 mmol of the solid ligand and the solution was boiled. When the solid $NaB(C_6H_5)_4$ was added (10 mmol), crystals were obtained immediately. The compound was recrystallized from butanol and chloroform.

$[Ni(NAs_3)I]B(C_6H_5)_4$.—A solution of 10 mmol of the ligand in 10 ml of absolute ethyl alcohol was added to a boiled solution of 10 mmol of anhydrous nickel iodide. On adding a solution of $NaB(C_6H_5)_4$ in the same solvent, crystals were obtained which were recrystallized from ethanol and chloroform.

Physical Measurements.—The absorption spectra were recorded in the range 4000–30,000 cm^{-1} with a Beckman DK-2 spectrophotometer and 1-cm silica cells. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment with magnesium oxide as the reference. The magnetic measurements were performed by the Gouy method with

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TABLE I

ANALYTICAL AND PHYSICAL DATA FOR THE NICKEL COMPLEXES

Compound	Color	Mp, °C	Λ_M, cm²/ohm mol[a]		n[b]	% C		% H		% Ni	
			$C_2H_4Cl_2$	$C_2H_5NO_2$		Calcd	Found	Calcd	Found	Calcd	Found
$[Ni(NAs_3)Br]B(C_6H_5)_4$	Green	207–208	17	47		63.75	63.80	5.03	5.10	4.72	4.77
$[Ni(NAs_3)I]B(C_6H_5)_4$	Blue	183–188	18	54		61.43	61.90	4.84	4.75	4.55	4.47
$Ni(AsNAs)Br_2$	Crimson	192–194	0.3	7	1.50	44.96	44.91	3.91	3.93	7.85	7.90
$Ni(AsNAs)I_2$	Dark gray	224–226	0.7	16	0.86	39.94	39.80	3.47	3.28	6.97	6.90
$Ni(AsOAs)I_2$	Dark brown	218–223	0.2	4		39.90	40.05	3.35	3.70	6.96	6.73
$Ni(AsSAs)I_2$	Green	216–217	1.1	15	0.85	39.15	39.49	3.29	3.39	6.83	6.71
$Ni(AsSAs)_2Br_2$	Light green	130–131	1.4	21	0.45	51.29	51.92	4.31	4.44	4.48	4.47
$Ni(AsC_2As)Br_2$	Purple	215–220	0.1			44.30	44.40	3.43	3.43	8.33	8.38
$Ni(AsC_2As)I_2$	Amethyst	200 dec	0.1	2	0.90	39.10	39.15	3.03	3.02	7.35	7.39
$Ni(AsC_4As)I_2$	Brown	199–203				40.67	41.90	3.41	3.72	7.10	7.03

[a] Molar conductance value of *ca.* 10^{-3} M solution of the compound in the two solvents. Reference values in nitroethane and dichloroethane, respectively, are 68 and 19 for $[(n\text{-}C_4H_9)_4N]Br$. [b] Ratio of the found to the theoretical molecular weight, for *ca.* 5×10^{-3} M solutions in dichloroethane.

the apparatus and experimental technique already described.[14] The sample tube was calibrated with $Co[Hg(SCN)_4]$ and freshly distilled water.[15] Diamagnetic corrections were calculated from Pascal constants.[15] Molecular weights were determined in 1,2-dichloroethane at 37° with a Mechrolab Model 301 A vapor pressure osmometer calibrated with benzil. Scale readings were made 3 min after a drop of the solution was placed on the thermistor. Concentrations of the solutions were *ca.* 5×10^{-3} M. The conductivity values were measured on a WTW Model LBR/B conductance bridge. Concentrations of the solutions were *ca.* 10^{-3} M.

Results

The compounds formed with the ligand I were isolated as tetraphenylborate salts $(NiLX)B(C_6H_5)_4$. The other compounds have either the formula $NiLX_2$ or NiL_2X_2. All of the compounds form air-stable crystals, soluble in polar solvents, such as nitro or chloro derivatives, except the complex $Ni(AsC_4As)I_2$ which is insoluble in any of these solvents. The analytical and physical data are given in Table I, the results of magnetic measurements are given in Table II, and details of the absorption bands in the region 5000–30,000 cm^{-1} are given in Table III.

TABLE II

MAGNETIC DATA FOR THE NICKEL COMPLEXES IN THE SOLID STATE

Compound	Temp, °C	$10^6\chi_g$, cgs units	$10^6\chi_M$, cgs units	μ_{eff}, BM
$[Ni(NAs_3)Br]B(C_6H_5)_4$	20	Diamagnetic		
$[Ni(NAs_3)I]B(C_6H_5)_4$	20	Diamagnetic		
$Ni(AsNAs)Br_2$	20	2.36	2140	2.25
$Ni(AsNAs)I_2$	20	Diamagnetic		
$Ni(AsOAs)I_2$	19	4.36	4330	3.19
$Ni(AsSAs)I_2$	20	Diamagnetic		
$Ni(AsSAs)_2Br_2$	20	2.62	4130	3.12
$Ni(AsC_2As)Br_2$	25	Diamagnetic		
$Ni(AsC_2As)I_2$	25	Diamagnetic		
$Ni(AsC_4As)I_2$	25	4.58	4190	3.17

Discussion

NAs_3 Complexes.—The complexes prepared with ligand I were $[Ni(NAs_3)X]B(C_6H_5)_4$ ($X = Br, I$). They are diamagnetic and behave as 1:1 electrolytes in 1,2-dichloroethane and nitroethane solution. The electronic spectra in solution or in the solid state show bands at *ca.* 13,000 and 17,500 cm^{-1} as well as a more intense band at 23,000–28,000 cm^{-1}. A comparison of these spectra with those obtained from complexes with similarly shaped ligands containing donor sets NP_3,[1] P_4,[3] As_4,[3,6] and PAs_3[4] would indicate that the complexes formed from the ligand I have a trigonal-bipyramidal structure. The position, shape, and intensities of the first two bands assigned as d–d bands are characteristic of this structure.[16] The frequencies of the NAs_3 complexes are much lower than those of the corresponding PAs_3[4] or As_4[3,6] complexes; a similar observation was made with the NP_3 type of complex.[1] This shift re-

TABLE III

THE MAXIMA AND EXTINCTION COEFFICIENTS FOR THE ELECTRONIC SPECTRA OF THE COMPLEXES

Compound	Solvent	Absorption max, cm^{-1} (ϵ_{molar} for soln)
$[Ni(NAs_3)Br]B(C_6H_5)_4$		13,000, 17,550
	$(CH_2Cl)_2$	13,000 (1050), 17,800 (566), 23,500 (2583)
$[Ni(NAs_3)I]B(C_6H_5)_4$		12,900, 17,250, 22,200 sh, 27,400 sh
	$C_2H_5NO_2$	12,820 (2430), 17,250 (1110), 22,200 sh
	$(CH_2Cl)_2$	12,820 (2580), 17,100 (1360), 22,200 sh, 27,400 (5250)
$Ni[AsSAs)I_2$		13,300 sh, 17,400
	$(CH_2Cl)_2$	13,000 sh, 17,400 (1700)
$Ni(AsNAs)I_2$		12,800 sh, 17,850
	$(CH_2Cl)_2$	17,650 (1130), 25,000 (3230)
$Ni(AsSAs)_2Br_2$		10,000, 14,700
	$(CH_2Cl)_2$	13,350 sh, 18,850 (1550)
$Ni(AsNAs)Br_2$		9800, 14,700 sh, 18,500
	$(CH_2Cl)_2$	9500 (26), 14,700 sh, 18,850 (600)
$Ni(AsOAs)I_2$		<5000, 8000 sh, 10,100, 15,870, 22,000
	$(CH_2Cl)_2$	9800 (485), 16,150 sh, 22,000 (4300)
$Ni(AsC_4As)I_2$		<5000, 8000 sh, 9750, 15,400 sh, 22,700
$Ni(AsC_2As)Br_2$		18,500, 26,000
	$(CH_2Cl)_2$	18,250 (765), 24,600 (670)
$Ni(AsC_2As)I_2$		17,400, 26,700 sh
	$(CH_2Cl)_2$	17,250 (1900)

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sults not only from the position of the apical N, P, or As atom in the spectrochemical series but also from the fact that the apical ligand atoms interact most with the d_{z^2} (a_1') orbital and therefore have the greater effect on the ground state $(a_1')^2$ (D_{3h} symmetry). Hence spectrochemical differences are magnified.

AsNAs and AsSAs Complexes.—Whereas the nickel iodide complexes of these ligands are diamagnetic, the nickel bromide complexes are paramagnetic. Ni(AsNAs)I_2 and Ni(AsSAs)I_2 are essentially nonelectrolytes and monomers in dichloroethane and nitroethane. Their diffuse reflectance spectra show a band at *ca.* 18,000 cm^{-1} with a shoulder at *ca.* 13,000 cm^{-1} (Figure 1), the frequencies of Ni(AsNAs)I_2 being higher than those of Ni(AsSAs)I_2, as expected.[17] These spectra are similar to that of Ni[$((CH_3)_2AsCH_2CH_2CH_2)_2AsCH_3$]$Br_2$ (12,500 (sh) and 21,000 cm^{-1} [18]) in whose case a distorted square-pyramidal structure has been established.[19] In dichloroethane the spectrum of Ni(AsSAs)I_2 is unchanged, and the spectrum of Ni(AsNAs)I_2 changes merely by the disappearance of the shoulder at 13,000 cm^{-1} (Figure 2). This change may be due to a small structural change or to the presence of a small amount of a square-planar species which would still be consistent with the conductivity data. Recently some spectra of low-spin pentacoordinate nickel complexes have been reported with only the band at *ca.* 20,000 cm^{-1}.[20]

Though it has generally been found that the absorption frequency of the main band is lower in pentacoordinate species than in square-planar species,[2,5,20] in the present instance the absorption frequencies of the complexes with donor-atom sets As_2NX_2 and As_2SX_2 are not very different from those of the square-planar complexes with donor sets As_2X_2 (see below). Clearly the relative donor strength of the fifth donor atom has a great effect on the energy levels.

The complex Ni(AsSAs)$_2$$Br_2$ has an effective magnetic moment of 3.10 BM. It is green, but through grinding it becomes dark purple. Also the fused compound is dark purple. Its reflectance spectrum has two bands at 10,000 and 14,700 cm^{-1} (Figure 3) and is characteristic of a distorted octahedral complex.[21] In dichloroethane the color change to dark purple and the spectrum are practically identical with those of the pentacoordinate complex of the same ligand with nickel iodide: a shoulder at 13,000 cm^{-1} and a main band at 18,000 cm^{-1} (Figure 3). One must conclude that in solution the compound dissociates into a pentacoordinate species Ni(AsSAs)Br_2 and free ligand. This is supported by the degree of the association which is 0.45 (Table I).

The compound Ni(AsNAs)Br_2 has an intermediate magnetic moment of 2.25 BM at room temperature which shows practically no variation between 79 and 293°K. The reflectance spectrum shows bands at 9800, 14,700 (sh), and 18,500 cm^{-1} (Figure 4). The first two bands are similar in frequency to those of the six-coordinate complex Ni(AsSAs)$_2$$Br_2$, while the more intense band at 18,500 cm^{-1} is characteristic of a dia-

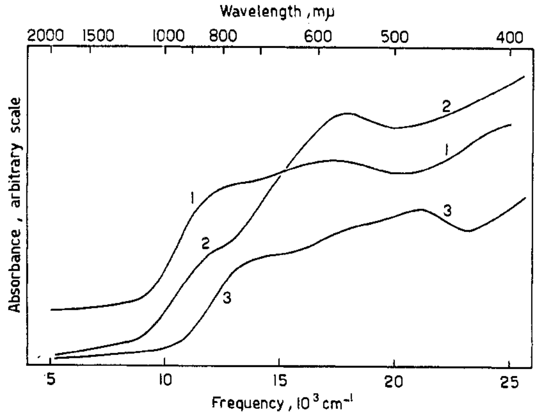

Figure 1.—Reflectance spectra of: 1, Ni(AsSAs)I_2; 2, Ni(AsNAs)I_2; 3, Ni[$((CH_3)_2AsCH_2CH_2CH_2)_2AsCH_3$]$Br_2$.

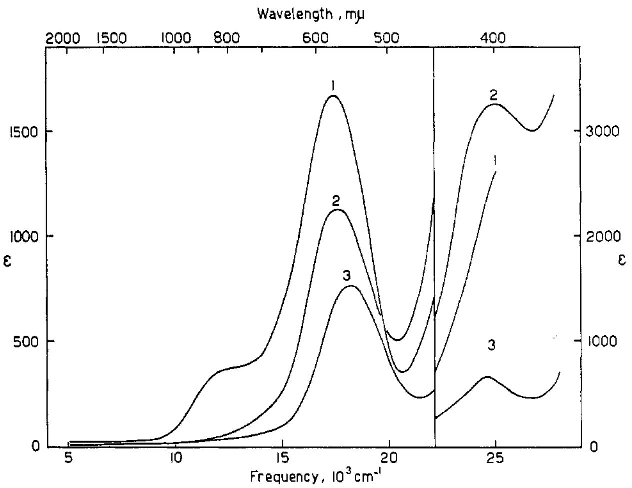

Figure 2.—Absorption spectra in 1,2-dichloroethane of: 1, Ni(AsSAs)I_2; 2, Ni(AsNAs)I_2; 3, Ni(AsC_2As)Br_2.

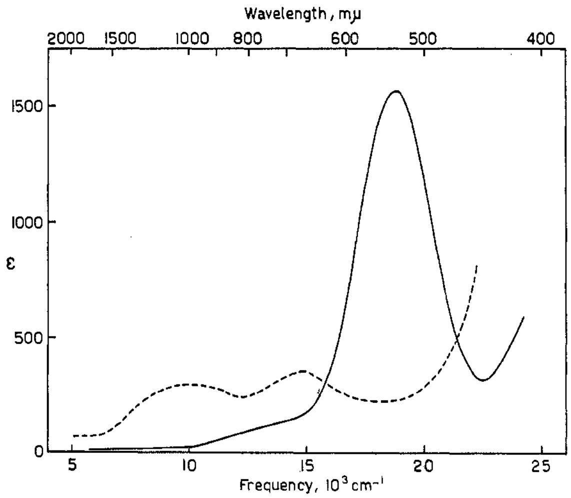

Figure 3.—Spectra of Ni(AsSAs)$_2$$Br_2$: reflectance spectrum, ------; absorption spectrum in 1,2-dichloroethane, ——.

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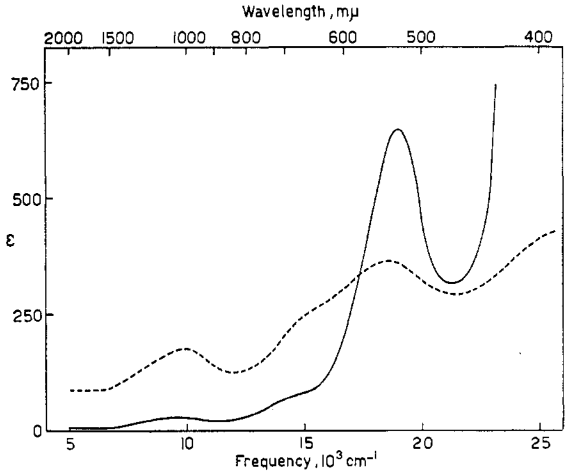

Figure 4.—Spectra of $Ni(AsNAs)Br_2$: reflectance spectrum, - - - - - -; absorption spectrum in 1,2-dichloroethane, ——.

magnetic species, and in fact the magnetic moment is in agreement with 50% of the nickel having μ_{eff} = 3.18 BM and 50% being diamagnetic. The dichloroethane solution spectrum is very similar to that of the solid. The compound in solution is a nonelectrolyte and the degree of association is 1.5 (Table I). A possible explanation is that the solid compound is dimeric $[Ni(AsNAs)Br_2]_2$ with a hexacoordinate paramagnetic nickel ion and a diamagnetic one. In solution the dissociation occurs to the extent that one dimeric molecule in three is dissociated. This dissociation would not affect the spectra because the diamagnetic monomer, probably $Ni(AsNAs)Br_2$, would absorb in the same region as the diamagnetic part of the dimer. Confirmation of the dissociation by means of magnetic measurements could not be obtained because of the low solubility of the compound.

AsOAs and AsC_nAs Complexes.—These complexes have the general formula $NiLX_2$ and are nonelectrolytes in dichloroethane and nitroethane. $Ni(AsOAs)I_2$ and $Ni(AsC_4As)I_2$ have effective magnetic moments of 3.19 and 3.17 BM, respectively. Of these, only the former complex is soluble. The properties of these compounds closely resemble those of the corresponding complexes in which phosphorus takes the place of arsenic;[22] a distorted tetrahedral structure was therefore assigned. The arsenic-containing compounds have practically identical spectra with bands at *ca.* 5000, 10,000, and 16,000 cm^{-1} (Figure 5) compared to 5000, 11,500, and 16,000 cm^{-1} for the corresponding phosphorus-containing compounds, and, again, the possibility that the insoluble compound Ni $(AsC_4As)I_2$ is polymeric with bridging diarsine groups cannot be entirely excluded.

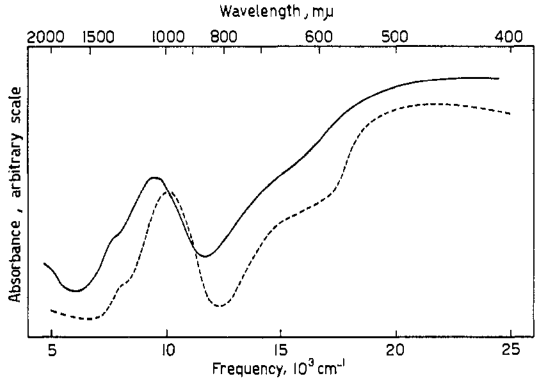

Figure 5.—Reflectance spectra of $Ni(AsC_4As)I_2$ (- - - - - -) and $Ni(AsOAs)I_2$ (——).

The complexes $Ni(AsC_2As)X_2$ (X = Br, I) are diamagnetic and have an absorption band at *ca.* 18,000 cm^{-1} ($\epsilon \simeq 1000$) and an additional band at 25,000 cm^{-1} (ϵ −670) in the case of bromide. The iodide, for which the molecular weight was measured, is essentially monomeric. A square-planar structure is therefore indicated for these complexes. Thus, the ω,ω'-bis(diphenylarsino)alkanes behave in the same way as the phosphine analogs, giving planar complexes when the donor atoms are separated by two methylene groups[23] and giving tetrahedral compounds when there are four methylene groups between them.[22]

Conclusions.—The effect of arsenic atoms in polyfunctional ligands on stereochemistry or magnetic properties is not changed much by the presence of other donor atoms. Pentacoordinate complexes in which the ligand donor set is As_4, As_3N, As_3, or As_2N are all diamagnetic as are the compounds containing sulfur also (ligand set As_2S). However, the oxygen atom in the ligand AsOAs does not coordinate to nickel, and a tetrahedral complex is formed instead, as with the analogous ligand without oxygen (AsC_4As).

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