Crystal Structure of Dibromodiadeniniumcopper(II) Dibromide: A Complex with Unidentate Adenine

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The crystal structure of the title compound has been determined from three-dimensional *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic with unit-cell dimensions $a = 18{\cdot}649$, $b = 8{\cdot}731$, $c = 12{\cdot}028$ Å, $\beta = 113{\cdot}14°$, space group *C*2/*c*, and $Z = 4$. Full-matrix least-squares refinement by use of 1657 independent reflections has reached *R* 0·056.

The structure contains complex cations $[Cu(adenineH)_2Br_2]^{2+}$ and bromide ions. In the complex cation the central copper atom lies on a diad and is co-ordinated to two N(9) atoms of unidentate adeninium ligands and to two terminal bromide atoms. The copper atom has a co-ordination intermediate between tetrahedral and square planar, with Cu–N 2·013 and Cu–Br 2·361 Å. The adenine molecule is protonated at N(1), and atoms N(1) and N(7) are involved in hydrogen bonding of the type N–H · · · Br⁻.

As part of a programme of crystallographic studies on transition-metal complexes with nucleotide bases we have determined the structure of a new copper–adenine (ade) compound prepared by Goodgame and Price.[1] The structure determination has shown it to have the formula $[Cu(adeH)_2Br_2]Br_2$. In this complex the adenine ligand is unidentate, co-ordinating *via* N(9), whereas in the other three copper–adenine complexes whose structures are known, the inner complex $[Cu(C_5H_4N_5)_2H_2O]_2,6H_2O$,[2] $[Cu(ade)_2Cl]_2Cl_2,6H_2O$,[3] and $Cu_3Cl_8(adeH)_2,4H_2O$,[4] adenine acts as a bridging ligand co-ordinating *via* N(3) and N(9). A preliminary account of this work has appeared.[5]

EXPERIMENTAL

Dibromodiadeniniumcopper(II) dibromide is obtained as dark brown prisms from copper(II) bromide and adenine (4 : 1 mole ratio) in aqueous acidic solution.

Crystal Data.—$C_{10}H_{12}Br_4CuN_{10}$, $M = 655{\cdot}2$, Monoclinic, $a = 18{\cdot}649(3)$, $b = 8{\cdot}731(2)$, $c = 12{\cdot}028(2)$ Å, $\beta = 113{\cdot}14(2)°$, $U = 1800{\cdot}9$ Å^3, $D_m = 2{\cdot}50$, $Z = 4$, $D_c = 2{\cdot}43$ g cm^{-3}, $F(000) = 1244$. Cu-K_α radiation $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 136·5 cm^{-1}. Preliminary Weissenberg photographs showed systematic absences *hkl*, $h + k = 2n + 1$, and *h*0*l* $l = 2n + 1$ consistent with space groups *Cc* or *C*2/*c*, the latter being shown to be correct from the subsequent solution and satisfactory refinement of the structure.

The single crystal used for the collection of intensity data was *ca.* 0·27 × 0·49 × 0·49 mm, and was mounted about the *b* axis on a Siemens off-line four-circle diffractometer. Cu-K_α radiation at a take-off angle of 4·5°, a nickel β filter, and a Na(Tl)I scintillation counter were used. Accurate unit-cell dimensions were obtained by measuring some high-angle α_1 and α_2 reflections. The intensities of 1657 independent reflections (to θ 70°) were measured by use of the θ—2θ scan technique with a ' five-value ' measuring procedure.[6] Of these 27 were judged to be unobserved, having a net count $<2{\cdot}58\sigma$ (*i.e.* below the 99% confidence level). The $0\bar{6}0$ reflection was measured as a reference every 40 reflections, and its net count did not vary noticeably during data collection (*ca.* 6 days). The data were scaled by use of the reference reflection and Lorentz and polarisation corrections were applied.

Solution and Refinement of the Structure.—The crystal structure calculations system ' *X*-ray '63 '[7] and its updated version,[8] were used for the solution and refinement of the structure. Calculations were carried out on the Imperial College IBM 7094 and CDC 6400 and the University of London CDC 6600 computers.

Considerable difficulty was encountered in interpreting the Patterson synthesis, owing to uncertainty about the

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[6] A. C. Skapski and P. G. H. Troughton, *Acta Cryst.*, 1970, **B26**, 716.

[7] ' *X*-Ray '63 ' system of programs, J. M. Stewart, University of Maryland Technical Report TR 64 6.

[8] Ref. 7, version of July 1970, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin.

stoicheiometry of the compound and the unexpected location of the copper atom on a diad axis. Eventually a correct solution was found, and least-squares refinement, using isotropic temperature factors, of the two bromine atoms in general positions and of the copper atom gave R 0·28. The resulting difference Fourier revealed the positions of all remaining non-hydrogen atoms and further isotropic refinement reduced R to 0·145. Six strong low-angle reflections were judged to be affected by extinction, and were removed from all subsequent refinement, and when atoms were allowed to refine with anisotropic thermal parameters R fell to 0·081. At this stage the data were corrected for absorption according to the method of Busing and Levy [9] by use of a 10 × 10 × 10 grid with pathlengths determined by the vector analysis procedure.[10] Refinement as previously gave R 0·058. All six hydrogen atoms were now located from a difference Fourier. They were included in subsequent refinement as a fixed-atom contribution with isotropic temperature factors of their parent atoms, and R was reduced to 0·056. Finally a weighting scheme of the type suggested by Hughes [11] was applied where $\omega = 1$ for $F < F^*$, $\sqrt{\omega} = F^*/F$ for $F \geqslant F^*$, with $F^* = 45$ found to be optimum. Although R remained unchanged, the standard deviations decreased by *ca.* 15%.

TABLE 1

Fractional co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
Cu(1)	0	−0·16521(14)	1/4
Br(1)	0·00760(4)	−0·34652(8)	0·39989(6)
Br(2)	0·27443(5)	0·23105(9)	0·19016(6)
N(1)	0·1413(4)	0·4099(7)	0·3311(5)
C(2)	0·1049(4)	0·3255(8)	0·2297(7)
N(3)	0·0789(3)	0·1865(7)	0·2280(5)
C(4)	0·0933(4)	0·1313(7)	0·3419(5)
C(5)	0·1314(4)	0·2085(7)	0·4474(6)
C(6)	0·1579(4)	0·3591(7)	0·4442(6)
N(7)	0·1332(3)	0·1137(7)	0·5400(5)
C(8)	0·0953(4)	−0·0120(8)	0·4856(6)
N(9)	0·0689(3)	−0·0096(6)	0·3669(5)
N(10)	0·1959(4)	0·4459(7)	0·5404(6)

TABLE 2

Anisotropic thermal parameters

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Cu(1)	242(5)	395(17)	284(11)	0	44(6)	0
Br(1)	309(3)	574(11)	379(7)	−66(4)	82(3)	104(5)
Br(2)	301(3)	748(12)	416(7)	159(4)	30(4)	−35(6)
	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
N(1)	26(2)	59(7)	51(5)	−5(3)	13(3)	2(5)
C(2)	25(3)	65(8)	47(6)	−2(4)	14(3)	5(5)
N(3)	25(2)	64(7)	31(4)	−2(3)	10(2)	2(4)
C(4)	16(2)	44(7)	29(5)	3(3)	5(2)	1(5)
C(5)	19(2)	56(8)	25(5)	4(3)	5(2)	3(5)
C(6)	17(2)	50(8)	43(5)	−1(3)	8(3)	−4(5)
N(7)	24(2)	62(7)	37(4)	−2(3)	3(2)	1(5)
C(8)	28(2)	57(8)	39(6)	−4(4)	10(3)	1(5)
N(9)	24(2)	42(6)	35(5)	−1(3)	10(2)	3(4)
N(10)	27(2)	83(8)	61(6)	−1(4)	11(3)	−18(6)

Full-matrix least-squares refinement was used throughout, and the function minimised was $\Sigma\omega(F_o - F_c)^2$. Atomic scattering factors were taken from ref. 12 and the real and imaginary parts of the anomalous dispersion correction for copper and bromine were taken from ref. 13. The final fractional co-ordinates of the non-hydrogen atoms and their estimated standard deviations are listed in Table 1, while Table 2 shows the coefficients in the expression for the anisotropic temperature factor $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The co-ordinates of the hydrogen atoms are given in Table 3. Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20594 (5 pp., 1 microfiche).*

TABLE 3

Fractional co-ordinates of the hydrogen atoms

Atom	x	y	z
H(1)[N(1)] *	0·167	0·504	0·313
H(2)[C(2)]	0·091	0·371	0·150
H(7)[N(7)]	0·153	0·123	0·621
H(8)[C(8)]	0·091	−0·100	0·536
H(101)[N(10)]	0·208	0·558	0·527
H(102)[N(10)]	0·223	0·365	0·597

* The atom listed in square brackets is that to which the hydrogen is attached.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The structure determination has proved that the title compound contains complex cations of formula $[Cu(adeH)_2Br_2]^{2+}$ and bromide ions. Figure 1 shows the shape of the dibromodiadeniniumcopper(II) ion, and also the thermal vibration ellipsoids [14] of the non-hydrogen atoms. The more important interatomic distances and angles are given in Table 4, and the arrangement of the ions in the unit cell is shown in Figure 2.

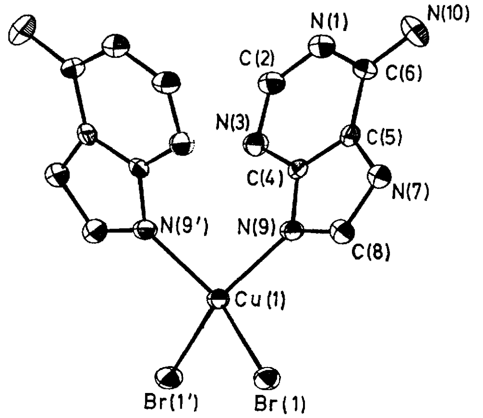

FIGURE 1 Structure of the $[Cu(adeH)_2Br_2]^{2+}$ ion. The thermal vibration ellipsoids are scaled to enclose 50% probability

The central copper atom of the complex cation lies on a diad axis and is four-co-ordinated. The adeninium ligands are unidentate, bonding *via* N(9), and the co-ordination is completed by two bromine atoms. The

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[9] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

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[11] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

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[13] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[14] C. K. Johnson, ORTEP Thermal Ellipsoid Plotting Program, Oak Ridge National Laboratory Report, ORNL 3794, 1965.

co-ordination geometry takes the form of a compressed tetrahedron. In a recent survey[15] Hathaway has shown that this is one of the less-common geometries for divalent copper (4 + 2 or 4 + 1 being most favoured). The extent of the distortion is severe: indeed the co-ordination is almost halfway between tetrahedral and square-planar. Because of the C_2 symmetry of the cation this flattening can be qualitatively visualised from Figure 2, and its extent is given by the angle (48·4°) between planes containing Cu,N(9),N(9′), and Cu,Br(1),Br(1′), which would be 90° for tetrahedral and 0° for square-planar co-ordinations. This distortion is greater than in the $\mathrm{CuBr_4}^{2-}$ ion in $\mathrm{Cs_2CuBr_4}$,[16] where the largest angle at the copper atom is 130·4°, whereas in the present compound it is 144·7° (see Table 4). The theory of such Jahn–Teller distortions has been extensively discussed.[17]

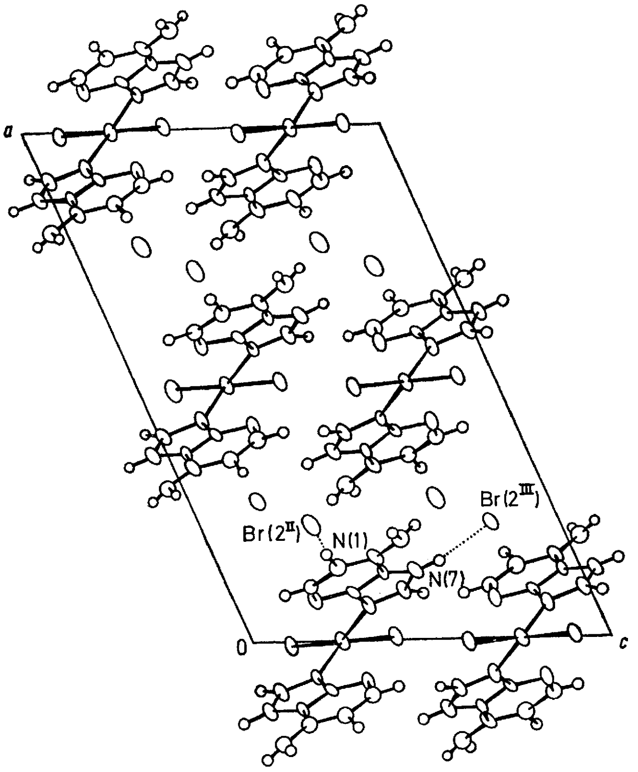

FIGURE 2 A [010] view of the crystal structure of $[\mathrm{Cu(adeH)_2Br_2}]\mathrm{Br_2}$. Because each complex cation is viewed down a two-fold axis the extent of flattening of the tetrahedral co-ordination is easily seen. The two hydrogen bonds (Table 4) are marked with a dotted line

The Cu–Br distances [2·361(1) Å] are at the short end of the known range, and are very similar to those found in $\mathrm{CuBr_4}^{2-}$ where the mean distance is 2·37 Å. The Cu–N distances [2·013(5) Å] are slightly, but not significantly shorter than in $[\mathrm{Cu(ade)_2Cl}]_2\mathrm{Cl_2,6H_2O}$ [mean 2·025(11)],[3] and $\mathrm{Cu_3Cl_8(adeH)_2,4H_2O}$ [mean 2·028(6) Å],[4] where the metal atom has a square-pyramidal (4 + 1) or octahedral (4 + 2) co-ordination. However, in a copper–guanine (gua) complex $\mathrm{Cu_2Cl_6(guaH)_22H_2O}$, where guanine is also unidentate, the Cu–N distance[18] [1·978(3) Å] is definitely shorter.

TABLE 4

Interatomic distances (Å) and bond angles (°) with standard deviations in parentheses

(*a*) Distances

Cu(1)–Br(1)	2·361(1)	Cu(1)–N(9)	2·013(5)
N(1)–C(2)	1·357(9)	C(6)–N(10)	1·331(9)
C(2)–N(3)	1·304(9)	C(5)–N(7)	1·377(9)
N(3)–C(4)	1·376(9)	N(7)–C(8)	1·329(8)
C(4)–C(5)	1·364(8)	C(8)–N(9)	1·315(9)
C(5)–C(6)	1·411(9)	N(9)–C(4)	1·385(8)
C(6)–N(1)	1·346(10)		

(*b*) Angles

Br(1)–Cu(1)–Br(1$^{\mathrm{I}}$)	95·81(5)	Br(1)–Cu(1)–N(9)	95·1(2)
N(9)–Cu(1)–N(9$^{\mathrm{I}}$)	95·1(2)	Br(1)–Cu(1)–N(9$^{\mathrm{I}}$)	144·7(2)
C(2)–N(1)–C(6)	124·4(6)	C(5)–C(4)–N(9)	109·4(6)
N(1)–C(2)–N(3)	124·8(7)	N(3)–C(4)–N(9)	125·1(5)
C(2)–N(3)–C(4)	112·7(6)	C(4)–C(5)–N(7)	107·1(6)
N(3)–C(4)–C(5)	125·4(6)	C(5)–N(7)–C(8)	105·0(6)
C(4)–C(5)–C(6)	119·7(6)	N(7)–C(8)–N(9)	114·9(7)
C(6)–C(5)–N(7)	133·2(6)	C(8)–N(9)–C(4)	103·6(5)
C(5)–C(6)–N(1)	113·0(5)	Cu(1)–N(9)–C(4)	128·5(4)
C(5)–C(6)–N(10)	125·4(7)	Cu(1)–N(9)–C(8)	127·7(5)
N(1)–C(6)–N(10)	121·6(6)		

(*c*) Hydrogen-bonded contacts

N(1) ··· Br(2$^{\mathrm{II}}$)	3·273(6)	N(7) ··· Br(2$^{\mathrm{III}}$)	3·309(5)
N(1)–H(1)–Br(2$^{\mathrm{II}}$)	168	N(7)–H(7)–Br($^{\mathrm{III}}$)	152

Superscripts refer to atoms in the following positions:

I $-x, y, \frac{1}{2} - z$ III $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$
II $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

By co-ordinating *via* N(9) only in the present compound, adenine behaves in a similar way to guanine in the two complexes whose structures have previously been determined, $\mathrm{Cu_2Cl_6(guaH)_2,2H_2O}$[18] and $\mathrm{ZnCl_3(guaH)}$.[19] On the other hand, in the only other metal complex known to involve unidentate adenine, $\mathrm{ZnCl_3(adeH)}$,[19] this ligand is bound to zinc *via* N(7).

A difference Fourier showed unambiguously that the adeninium ligand is protonated at N(1), and further evidence in support of this arises from the work of Singh.[20] On the basis of a survey of a large number of heterocyclic compounds containing six-membered-ring nitrogen he was able to show that where the nitrogen is protonated the angle C–N–C is 125 ± 3°, and where no hydrogen is attached this angle is 116 ± 3°. In all three copper–adenine complexes which we have studied we find this observation to be true. Thus in the present compound the angle at N(1) is 124·4(6)°, and in $\mathrm{Cu_3Cl_8(adeH)_2,4H_2O}$ it is 124·3(1·0)°, whereas in $[\mathrm{Cu(ade)_2Cl}]_2\mathrm{Cl_2,6H_2O}$, in which this nitrogen is not protonated, the angle is 116·9(1·3)°.

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Table 5 compares the bond lengths and angles found[4,19,21,22] in adenine-containing molecules, where the adenine is protonated at N(1). (For one of these structures the bond angles are not yet available.) In making the comparison one has to bear in mind the estimated standard deviations and the fact that in general the differences between bonds in the same adenine group are small, and also that there may exist genuine differences between the same bonds in different compounds. Nevertheless some features appear to be constant. Thus N(3)–C(2), N(7)–C(8), and N(10)–C(6) are short (mean 1·31—1·32 Å), and N(3)–C(4) > N(3)–C(2) and N(7)–C(5) > N(7)–C(8). In the case of the two C–C bonds, C(5)–C(6) is longer than C(4)–C(5), and is in all cases the longest bond in the adenine group (mean 1·41 Å). Other bonds fall in an intermediate category or else seem to be sensitive to the ligand attached, notably those involving N(9) which is linked to copper (*A*, *B*), hydrogen (*C*), or glycosidic carbon (*D*, *E*). As regards the angles, those in the two copper complexes show very close concordance, and similarly in the case of the two AMP molecules. The main difference between the two pairs involves angles centred on C(4) and C(5).

TABLE 5

Comparison of bond lengths (Å) and bond angles (°) found in structures containing adenine protonated at N(1)

		A	*B*	*C*	*D*	*E*
Bond	$\bar{\sigma}$	0·013	0·009	0·007	0·012	0·006
N(1)–C(2)		1·32	1·36	1·36	1·37	1·35
C(2)–N(3)		1·33	1·30	1·28	1·31	1·31
N(3)–C(4)		1·38	1·38	1·36	1·34	1·35
C(4)–C(5)		1·37	1·36	1·38	1·40	1·38
C(5)–C(6)		1·39	1·41	1·42	1·45	1·40
C(6)–N(1)		1·38	1·35	1·36	1·36	1·36
C(6)–N(10)		1·32	1·33	1·30	1·31	1·32
C(5)–N(7)		1·38	1·38	1·39	1·36	1·38
N(7)–C(8)		1·32	1·33	1·31	1·33	1·31
C(8)–N(9)		1·33	1·32	1·34	1·40	1·37
N(9)–C(4)		1·36	1·39	1·35	1·38	1·36
Angle	$\bar{\sigma}$	0·9	0·6		0·8	0·3
C(2)–N(1)–C(6)		124	124		123	123
N(1)–C(2)–N(3)		125	125		126	126
C(2)–N(3)–C(4)		113	113		112	112
N(3)–C(4)–C(5)		123	125		129	127
C(4)–C(5)–C(6)		122	120		116	118
C(5)–C(6)–N(1)		113	113		115	114
C(5)–C(6)–N(10)		125	125		124	126
N(1)–C(6)–N(10)		122	122		122	120
C(5)–C(4)–N(9)		110	109		104	105
C(4)–C(5)–N(7)		107	107		112	111
C(5)–N(7)–C(8)		105	105		103	103
N(7)–C(8)–N(9)		114	115		112	113
C(8)–N(9)–C(4)		104	104		107	107

A, $Cu_3Cl_8(adeH)_2,4H_2O$,[4] bonded to copper *via* N(3) and N(9). *B*, title compound, bonded to copper *via* N(9). *C*, $ZnCl_3(adeH)$,[19] bonded to zinc *via* N(7). *D*, Adenosine-5′-phosphate (5′ AMP),[21] bonded to glycosidic carbon *via* N(9). *E*, Adenosine-3′-phosphate,$2H_2O$ (3′AMP),[22] bonded to glycosidic carbon *via* N(9).

The complex cations and the bromides ions are linked by a pattern of hydrogen bonds of the type N–H · · · Br^-. Atoms N(1) and N(7) are clearly involved, and are 3·27 and 3·31 Å from the free ion. The angles N–H–Br are in both cases compatible with hydrogen bonding (see Table 4). Each bromide ion has two such links, and the angle H–Br–H is *ca.* 112°. For comparison, in 9-methyladenine dihydrobromide[23] N(1), N(10), and N(7) are 3·13, 3·22, and 3·28 Å from bromide ions.

A least-squares calculation shows that the adeninium ligand is satisfactorily planar (maximum deviation *ca.* 0·03 Å). Table 6 shows the deviation of individual adenine atoms from this plane and also of three atoms not defining the plane *viz.* the bonded copper atom and the two bromide ions which are hydrogen-bonded to this particular ligand. The deviation of the copper atom represents a distortion at N(9) of *ca.* 7° out of the plane (if one assumes that the adenine is strictly planar).

TABLE 6

Deviations (Å) of relevant atoms from the least-squares test plane of the adeninium ligand

Plane: N(1), C(2), N(3), C(4)—(6), N(7), C(8), N(9), N(10)
Equation: $17{\cdot}2x - 3{\cdot}30y - 3{\cdot}78z = -0{\cdot}14$
Deviations: N(1) 0·031, C(2) −0·003, N(3) −0·020, C(4) −0·019, C(5) −0·022, C(6) 0·004, N(7) −0·017, C(8) 0·015, N(9) 0·030, N(10) 0·000, Cu(1) 0·262, Br(2^{II}) −0·441, Br(2^{III}) −0·077

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