

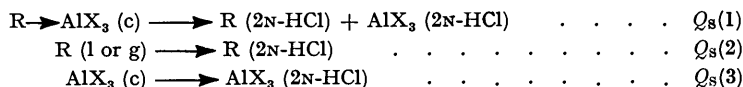
*Aluminium Halide Complexes with Pyridine, Trimethylamine,
and Triethylamine. Part II.**

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Heats of solution have been measured, and dissociation energies calculated, for seven crystalline 1 : 1 complexes, C_5H_5N, AlX_3 and Me_3N, AlX_3 (where X = Cl, Br, or I) and $Et_3N, AlCl_3$. The heat of solution found for AlI_3 (c) of 135 ± 0.8 kcal. is much greater than the previously accepted value of 89. The dissociation energies are used in a discussion of heats of mixing of donor and halide molecules, and to decide whether there is only one ligand. The dissociation energies observed are larger for these AlI_3 complexes than for those with $AlBr_3$ and $AlCl_3$, and this is attributed to a relatively small reorganisation energy of the AlI_3 radical, the actual N→Al bond-dissociation energy being approximately constant in all cases. Values for the aluminium-halogen bond energies are calculated and discussed.

THIS paper describes the results of a determination of dissociation energies for the seven crystalline 1 : 1 complexes involving the N→Al link described in Part I.* Heats of solution of a given complex, and its component donor and acceptor molecules, have been determined in 2N-hydrochloric acid.



Then, for the dissociation in the condensed phase,



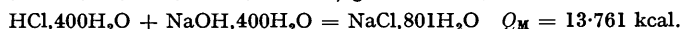
we define a dissociation energy D_c (heat, $-D_c$), which is therefore given by

$$D_c = Q_s(2) + Q_s(3) - Q_s(1)$$

EXPERIMENTAL

The complexes were available in sealed, evacuated, glass bulbs, each holding about 0.1 g. The calorimeter used was the thermistor calorimeter described by Dilke, Eley, and Sheppard (*Trans. Faraday Soc.*, 1950, **46**, 261), with a bulb-breaking attachment fitted in place of the liquid delivery tube. Each experiment consisted in breaking a bulb of complex under 100 ml. of 2N-hydrochloric acid, and was followed by electrical calibration by passage of a known current through a coil of "Bright-ray" wire of resistance 20.32 Ω. All measurements were at 25°.

Before examination of the complexes, the calorimeter was checked by a determination of the heat of neutralisation. Four experiments were made in which accurately known amounts (0.5—1 ml.) of 5N-hydrochloric acid, contained in bulbs, were broken under 100 ml. of 0.05N-sodium hydroxide. The heat of neutralisation calculated by the least squares method was 14.6 kcal./mole, with a probable error of 0.2 kcal. Richards and Rowe (*J. Amer. Chem. Soc.*, 1920, **42**, 1621; 1921, **43**, 770; 1922, **44**, 684) give, for 20°,



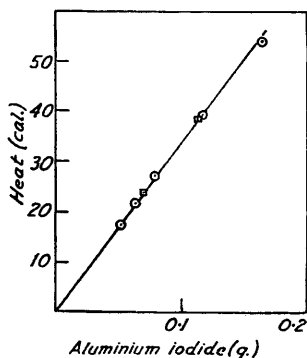
To this we add a heat of dilution of 1.2 kcal./mole for the hydrochloric acid, those for sodium hydroxide and sodium chloride being negligible, and subtract 0.275 kcal. for the temperature effect on the heat of reaction. The result is then 14.7 kcal./mole, in agreement with our observed values. The estimated accuracy of the measurements is 1%.

RESULTS

Usually five determinations were made with each substance, with different weights, and 100 ml. of 2N-hydrochloric acid. The results were plotted as heat evolved against weight of substance, and the best straight line was drawn by the method of least squares. The slope gave the heat of solution per gram of substance, which was converted into the heat of solution per mole (for the aluminium halides, the molecular weight of the monomer AlX_3 was used here).

* Part I, *J.*, 1952, 1914.

The results are given in Table 1, values for the individual experiments being listed in the thesis of H. Watts (Bristol, 1952). An example of the procedure, for the case of aluminium iodide, is shown in the Figure.



The heat of solution of aluminium iodide in water (squares) and in 2*N*-hydrochloric acid (circles).

TABLE 1. *Heats of solution, Q_s , and dissociation energies (condensed phase), D_C , at 25°.*

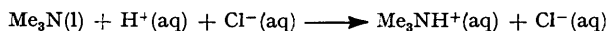
Substance	No. of expts.	Q_s (kcal./mole)	D_C (kcal./mole)	Substance	No. of expts.	Q_s (kcal./mole)	D_C (kcal./mole)
AlCl ₃ (c)	6	77.5 ± 0.6	—	AlI ₃ (c)	7 *	135 ± 0.8	—
C ₆ H ₅ N, AlCl ₃ (c)	6	54.5 ± 0.8	31.8	C ₆ H ₅ N, AlI ₃ (c)	4	68.7 ± 1.2	75.1
Me ₃ N, AlCl ₃ (c)...	5	63.6 ± 0.9	30.8	Me ₃ N, AlI ₃ (c)	4	75.2 ± 1.6	76.7
Et ₃ N, AlCl ₃ (c)	5	69.3 ± 1.7	28.5				
AlBr ₃ (c)	5	86.5 ± 0.5	—	C ₆ H ₅ N (l)	3	8.8 ± 0.2	—
C ₆ H ₅ N, AlBr ₃ (c)	5	63.4 ± 0.7	31.9	Me ₃ N (l)	6	16.9 ± 0.2	—
Me ₃ N, AlBr ₃ (c)	5	70.4 ± 1.0	33.0	Et ₃ N (l)	5	20.3 ± 0.7	—

* Two of these experiments were with water as solvent and agreed with those with 2*N*-HCl (cf. Figure).

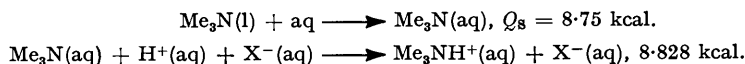
DISCUSSION

First we compare our values of Q_s with those available in the literature.

The Aluminium Halides.—The heats of solution obtained by us agree closely with earlier values in the cases of aluminium chloride and bromide, but there is a large discrepancy in the case of the iodide. Thus, for aluminium chloride, Bichowsky and Rossini ("Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, 1936) list four values of the heat of solution in water, averaging 77.2 ± 0.9 kcal./mole, and, in addition, there are values of 78.09 (H₂O) and 78.59 (0.02*N*-HCl) (Roth and Buchner, *Z. Elektrochem.*, 1934, **40**, 87), 71.7 ± 0.1 (0°; 20% HCl) (Klemm and Tanke, *Z. anorg. Chem.*, 1931, **200**, 343), and 79.4 kcal. (H₂O) (Roth and Börger, *Z. Elektrochem.*, 1938, **44**, 540). For aluminium bromide, Bichowsky and Rossini give values of 85.3 and 90.0, and Klemm and Tanke 89.9 (0°; 20% HCl). There appear to be only two values available for aluminium iodide, 89.0 (9°; H₂O) (Berthelot, see Landolt-Börnstein, "Tabellen," Vol. II, p. 1554) and 89.9 (0°; 20% HCl) (Klemm and Tanke, *loc. cit.*). These values are very much smaller than the 135 kcal./mole found in this work, and the difference is much too large to arise from differences in the conditions of experiment, such as temperature or acid concentration. Two probable causes for the earlier values are impurities in the aluminium iodide used, and incomplete dissolution. The only cause for too high a value for the heat of solution would be an error in the electrical calibration of the calorimeter. This is ruled out, first by the good reproducibility of the experiments with aluminium iodide, and secondly by checks on the calorimeter before and after the aluminium iodide runs. The checks "before" consist not only in the heats of neutralisation, but also in the heats of solution of the chloride and bromide. The check "after" consists in the value for the heat of solution of trimethylamine of 16.9 kcal. This corresponds to the reaction



The following data are available :

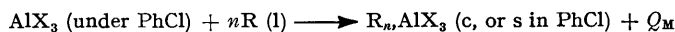


The first figure is from the International Critical Tables (Vol. V, p. 149), and the second from Everett and Wynne-Jones (*Trans. Faraday Soc.*, 1939, 35, 1380). The sum of these gives 17.58 kcal., which agrees with our value, within uncertainties arising from heats of dilution, differences in anions, etc.

Taking our heats of solution, and the other necessary data from Bichowsky and Rossini (*op. cit.*), we obtain the following values for the heats of formation of the aluminium halides at 25° from the elements in their standard states (figures given by Bichowsky and Rossini are in parentheses) :

$$\begin{aligned} Q_f [\text{AlCl}_3 (\text{c})] &= 167.9 \text{ kcal./mole (166.8)} \\ Q_f [\text{AlBr}_3 (\text{c})] &= 125.8 \text{ kcal./mole (126.7)} \\ Q_f [\text{AlI}_3 (\text{c})] &= 31.4 \text{ kcal./mole (77.2)} \end{aligned}$$

Heats of Mixing.—A considerable number of measurements of heats of mixing of donor with aluminium halide in the presence of chlorobenzene as diluent have been made in this laboratory (Dilke, Eley, and Sheppard, *Trans. Faraday Soc.*, 1950, 46, 261; D. J. A. Dear, Thesis, Bristol, 1951). These correspond to the reaction



While there is some uncertainty in the initial and the final state, *i.e.*, whether crystalline or in solution, the main uncertainty which affects interpretation of Q_{M} lies in the value of n , excess of the donor R being used. We may now compare values of Q_{M} with values of D_{C} in certain cases and thus throw light on the value of n . We have

$\text{C}_5\text{H}_5\text{N}, \text{AlCl}_3$	$Q_{\text{M}} = 47.8$ (Dilke <i>et al.</i>)	$D_{\text{C}} = 31.8$
$\text{Et}_3\text{N}, \text{AlCl}_3$	$Q_{\text{M}} = 42.6$ (Dear, <i>loc. cit.</i>)	$D_{\text{C}} = 28.5$
$\text{C}_5\text{H}_5\text{N}, \text{AlBr}_3$	$Q_{\text{M}} = 24.0$ (Dilke <i>et al.</i>)	$D_{\text{C}} = 31.9$
$\text{C}_5\text{H}_5\text{N}, \text{AlI}_3$	$Q_{\text{M}} = 60.1$ (Dear)	$D_{\text{C}} = 75.1$

The agreement is reasonable enough in cases two and four to allow us to conclude that here n , the number of ligand molecules, is restricted to unity. In the first case, the discrepancy indicates that further molecules of donor are taken up beyond $n = 1$, probably by weak dipole forces. In support of this view we have found it possible to prepare a crystalline complex, of m. p. 15°, by addition of excess of pyridine to aluminium chloride in the presence of benzene. The analysis and molecular weight of this complex corresponded to $3\text{C}_5\text{H}_5\text{N}, \text{AlCl}_3, 3\text{C}_6\text{H}_6$, and it was possible to remove considerable amounts of first benzene, then pyridine, by pumping *in vacuo*.

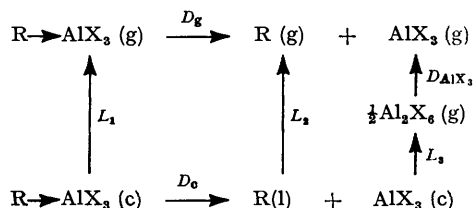
Fisher-Hirschfelder models show that the bulky triethylamine molecule effectively screens the aluminium atom from accepting more than one donor molecule, while the flat pyridine molecule, if held by the nitrogen atom, should permit further pyridine molecules to approach the aluminium atom to be held by dipole forces. This probably explains the difference between $\text{Et}_3\text{N}, \text{AlCl}_3$ ($n = 1$) and $(\text{C}_5\text{H}_5\text{N})_n, \text{AlCl}_3$ ($n > 1$). With $\text{C}_5\text{H}_5\text{N}, \text{AlI}_3$, the iodine atoms, being much larger than bromine or chlorine, will tend to restrict additional donor molecules from approaching the aluminium, although by itself this effect is probably too small to be decisive. In addition, we expect a smaller positive charge on the aluminium atom for the bromide and iodide than for the chloride. From electronegativities it is possible to estimate bond moments for AlCl 4.0 D, AlBr 3.2 D, and AlI 1.4 D; and we should, therefore, expect the tendency for dipolar addition to fall in this order, as observed. Higher complexes, such as $3\text{C}_5\text{H}_5\text{N}, \text{AlBr}_3$ reported by Müller (*Z. anorg. Chem.*, 1926, 156, 65) and Jacober and Kraus (*J. Amer. Chem. Soc.*, 1949, 71, 2705) support this suggestion for aluminium bromide.

The N→Al Bond Dissociation Energy. Dissociation of the Solid Complex into Gaseous Components.—It is possible to analyse the dissociation energy in the condensed phase, D_{c} , so as to obtain $D(\text{N} \rightarrow \text{Al})$, the dissociation energy of the N→Al bond, on the basis of certain

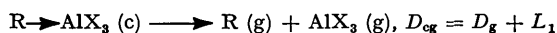
reasonable assumptions. Consider D_g , the dissociation energy of the complex in the gas phase into donor and monomer aluminium halide, given by

$$D_g = L_2 + D_{\text{AlX}_3} + L_3 + D_c - L_1$$

where the energy terms are defined by the cycle below



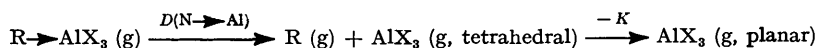
To obtain D_g from D_c requires a knowledge of L_1 , the latent heat of sublimation of the complex, which is not available for our complexes. Klemm, Clausen, and Jacobi (*Z. anorg. Chem.*, 1931, **200**, 363) found the following values of L_1 for the ammonia complexes: $\text{NH}_3, \text{AlCl}_3$ 20 kcal./mole; $\text{NH}_3, \text{AlBr}_3$ 21 kcal./mole; $\text{NH}_3, \text{AlI}_3$ 22 kcal./mole. This suggests that L_1 varies very little from chloride to bromide, so that we may usefully discuss the quantity $D_g + L_1$, which is the dissociation energy of the crystalline complex into gaseous components, D_{cg} , viz.:



Values of D_{cg} for the complexes are listed in the first part of Table 2. Values of L_3 used are: AlCl_3 13.5, AlBr_3 9.7, and AlI_3 12.1 kcal., and those of D_{AlX_3} are: AlCl_3 14.5, AlBr_3 13.3, and AlI_3 11.3 kcal. (Fischer and Rahlfs, *ibid.*, 1932, **205**, 1). Values used for L_2 are 8.5 kcal./mole for pyridine (Mathews, *J. Amer. Chem. Soc.*, 1926, **48**, 562), 5.7 for trimethylamine (Swift and Hochandel, *ibid.*, 1945, **67**, 880), and 7.9 for triethylamine (Thompson and Linnett, *Trans. Faraday Soc.*, 1936, **32**, 681).

The N→Al Bond Dissociation Energy.—(a) *Variation with donor.* Reference to the D_{cg} values in the first part of Table 2 shows a small decrease over the series $\text{C}_5\text{H}_5\text{N} > \text{Me}_3\text{N}, \text{Et}_3\text{N} > \text{NH}_3$. The work of H. C. Brown and his colleagues has established the following D_g values for the dissociation of gaseous trimethylboron complexes: Me_3N 17.62, pyridine 17, NH_3 13.75, and Et_3N probably <10 kcal. (*J. Amer. Chem. Soc.*, 1944, **66**, 435; 1947, **69**, 1137, 1332). Our results show a relatively high value for pyridine for D_{cg} ($= D_g + L_1$) which may be a result of a somewhat higher value for the latent heat of sublimation L_1 , although this is not by any means certain, as the pyridine complexes had the lowest melting point (cf. Part I) of those examined. The main difference concerns the triethylamine complex, and we are led to postulate that the steric forces which Brown and Taylor (*loc. cit.*, p. 1332) show to be responsible for the low heat with trimethylboron, are much smaller with aluminium chloride. This is what one would expect, as the B-C bond is only 1.56 Å in trimethylboron (Levy and Brockway, *ibid.*, 1937, **59**, 2085) compared with Al-Cl 2.06 Å (Palmer and Elliot, *ibid.*, 1938, **60**, 1852), so that there will be more crowding of groups attached to the donor and acceptor atoms.

(b) *Variation over series chloride to iodide.* For a discussion of this variation it would be desirable to know D_g , the dissociation energy of the gaseous complex. We may consider this process to occur in two stages, with the energy steps



and to involve a dissociation energy of the N→Al bond followed by a reorganisation energy K of the AlX_3 radical, so

$$D_g = D(\text{N} \rightarrow \text{Al}) - K$$

The reorganisation energy K was introduced for boron fluoride-ether complex by Bauer, Finlay, and Laubengayer (*J. Amer. Chem. Soc.*, 1943, **65**, 889). For the aluminium halides we may estimate K by a method given in the Appendix, and it is found to decrease

strongly over the series chloride to iodide : AlCl_3 , 79.5, AlBr_3 65.7, AlI_3 35.7 kcal. This behaviour may account very largely for the observed values of D_{cg} . Thus

$$D(\text{N} \rightarrow \text{Al}) = D_g + K$$

$$D(\text{N} \rightarrow \text{Al}) + L_1 = D_g + L_1 + K = D_{\text{cg}} + K$$

and we obtain the results shown in the second part of Table 2. It is clear that while D_{cg} varies greatly over the series chloride to iodide, the quantity $[D(\text{N} \rightarrow \text{Al}) + L_1]$ remains nearly constant. Taking the values for the ammonia complexes, and using

TABLE 2. *Dissociation energy of complexes.*

Ligand	D_{cg} (kcal.) ¹			$D(\text{N} \rightarrow \text{Al}) + L_1^2$ (kcal.)		
	AlCl_3	AlBr_3	AlI_3	AlCl_3	AlBr_3	AlI_3
$\text{C}_5\text{H}_5\text{N}$	68.3	63.4	107.0	148	129	143
Me_3N	64.5	61.7	105.8	144	127	141
Et_3N	64.4	—	—	144	—	—
NH_3	60.0	62.0	100.0	139	128	136

¹ $D_{\text{cg}} = D_g + L_1$, *i.e.*, solid complex \rightarrow gaseous components. ² $D(\text{N} \rightarrow \text{Al}) + L_1 = D_{\text{cg}} + K = D_g + L_1 + K$. ³ Klemm, Clausen, and Jacobi (*loc. cit.*) give the following D_c values; $\text{NH}_3, \text{AlCl}_3$ 32; $\text{NH}_3, \text{AlBr}_3$ 39; $\text{NH}_3, \text{AlI}_3$ 32. We accept the first two, but change the last to 77, as a result of taking the heat of solution of AlI_3 (c) as 135 instead of 78.9. The D_{cg} values are calculated from these D_c values for comparison with our own data, although Klemm *et al.* obtained L_1 and hence D_g values, which are more fundamental than D_{cg} .

the L_1 already given, we obtain $D(\text{N} \rightarrow \text{Al})$ values of 118, 107, and 114 kcal. for the chloride, bromide, and iodide respectively, *i.e.*, an average value of 113 kcal. for the three halides. The $[D(\text{N} \rightarrow \text{Al}) + L_1]$ values for the other bases are higher than for the ammonia complexes, but the L_1 values would also be expected to be higher, and to vary little over the halide series. Therefore it seems reasonable to suggest the following two conclusions: $D(\text{N} \rightarrow \text{Al})$ is (a) nearly constant over all the complexes examined, and (b) approximately 113 kcal. Conclusion (b) is more speculative than conclusion (a), and since the K values used in the calculations are upper values (cf. Appendix 2), the figure 113 will also be an upper value. However, it scarcely seems likely that $D(\text{N} \rightarrow \text{Al})$ will fall below 90 kcal. and the result that $D(\text{N} \rightarrow \text{Al})$ lies in the range 90—113 kcal. remains of great interest. An interesting future problem is now to see whether such a magnitude can be justified on theoretical grounds.

APPENDIX

1. *Bond Energy of Aluminium-Halogen Bonds.*—We write $E(\text{Al-X})$, the bond energy of Al-X , as $\frac{1}{3}Q_{\text{fg}}$, where Q_{fg} is the heat of formation of AlX_3 monomer from Al and X atoms in the gas phase:

$$Q_{\text{fg}} = Q_t + 55 + \frac{3}{2}L_4 - D_{\text{AlX}_3} - L_3$$

where Q_t , D_{AlX_3} , and L_3 are defined (values given earlier in this paper), 55 kcal. is the heat of sublimation of aluminium, and L_4 is the energy change of the process X_2 (c, l, or g) \rightarrow $2\text{X}(g)$, taken from Bichowsky and Rossini (*op. cit.*).

As a matter of interest, we also consider AlF_3 , taking $Q_t = 311$ kcal. (quoted by Irmann, *Helv. Chim. Acta*, 1950, **33**, 1449), $L_3 = 59$ kcal., and, since double molecules are not formed, $D_{\text{AlF}_3} = 0$ and $L_4 = 63.5$ kcal. (Naryshkin, *Chem. Abs.*, 1940, **34**, 1237). Bond energies so calculated are listed as $E(\text{Al-X})$ obs. in Table 3.

TABLE 3. *Bond energies, kcal./mole.*

Bond	Al-F	Al-Cl	Al-Br	Al-I
$E(\text{Al-X})$ obs.	134	94	79	47
$E(\text{Al-X})$ calc.	194	99	80	55

We have also calculated values of $E(\text{Al-X})$ by using Pauling's equation, together with his values for single-bond energies and electronegativities ("Nature of the Chemical Bond," Cornell University Press, New York, 1939, p. 60) and with the assumption that $E(\text{Al-Al}) = \frac{2}{3}S$, where S is the sublimation energy, which assumes that in the sublimation we have to break 3 covalent bonds each involving 2 atoms. Pauling has apparently based his electronegativity value for Al on this assumption (*op. cit.*, p. 63), applied to an unstated compound or compounds of aluminium. (We are essentially dealing with an empirical procedure.) The results in

Table 3 seem to justify the method *a posteriori*, except for the case of Al-F. It seems likely that Pauling's electronegativity value of 4.0 for fluorine is too high; a lower value would also be consonant with the suggestion of Evans, Warhurst, and Whittle (*J.*, 1950, 1524), that the electron affinity of the element is less than that of chlorine.

2. *Estimate of Reorganisation Energy, K.*—Consider the energy of the process, $\text{Al}_2\text{X}_6 \longrightarrow 2\text{AlX}_3$, $2D_{\text{AlX}_3}$. The initial process is the rupture of two Al-X bridge bonds $(\text{Al-X})_b$, followed by the change tetrahedral to planar in the AlX_3 radicals, therefore

$$2D_{\text{AlX}_3} = 2D(\text{Al-X})_b - 2K$$

We now assume that $D(\text{Al-X})_b$ may be approximated by $E(\text{Al-X})$ given in Table 3, *i.e.*, we equate the energy of the Al-X bridge bond to that of the normal bond. Palmer and Elliott (*loc. cit.*) show the former to be longer than the latter, the differences in length being 0.15 Å for the chloride, 0.12 Å for the bromide, and 0.05 Å for the iodide. Thus the bridge bonds are probably very little weaker than the normal bonds, for example, in the extreme case of Al-Cl by only 2.6 kcal. The force constant of the Al-Cl bond is 1.6×10^6 dynes/cm. (Kohlrausch and Wagner, *Z. physikal. Chem.*, 1942, 52, 185), so the energy required to stretch it by 0.15 Å is only this amount. With this assumption and using the known D_{AlX_3} values (Fischer and Rahlfs, *loc. cit.*), we calculate

$$K(\text{AlCl}_3) = 79.5; K(\text{AlBr}_3) = 65.7; K(\text{AlI}_3) = 35.7 \text{ kcal.}$$

Because of the above assumptions, these values will be upper limits for the reorganisation energies, but should faithfully reflect the differences between the chloride, bromide, and iodide.

Note added in proof.—By using data from the "Tables of Selected Values of Chemical Thermodynamic Properties" (Nat. Bur. Standards, Washington, Circular 500, 1952) and our values of the heats of solution, we obtain $Q_f[\text{AlCl}_3(\text{c})] = 168$; $Q_f[\text{AlBr}_3(\text{c})] = 125.6$; $Q_f[\text{AlI}_3(\text{c})] = 30.5$ kcal./mole. Differences in the figures shown in Table 3 arise mainly from the new values of the dissociation energy of fluorine and the heat of sublimation of aluminium. The values of K thus become 86, 73, and 42 for chloride, bromide, and iodide respectively, and the value of $D(\text{N-Al})$ is raised by ~ 6 kcal.

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