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Binuclear Rhodium(I) Complexes of Aromatic Azines and Crystal Structure of Salicylaldazinotetracarbonyldirhodium, $C_{18}H_{10}N_2O_6Rh_2$*

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Abstract

Reaction of the dimer $[Rh(CO)_2Cl]_2$ or $Rh(PPh_3)_3Cl$ with disodium derivative of potential tetradentate azines gave dirhodium derivatives $[Rh(CO)_2]_2$(azine) or $[Rh(PPh_3)_2]_2$(azine). The complexes were isolated and characterised spectroscopically. The structure of the complex $[Rh(CO)_2]_2$(salicylaldazine) was determined by single crystal X-ray diffraction technique. The crystals are orthorhombic, space group *Pbnn*, $a = 10.480(2)$, $b = 15.831(2)$ and $c = 22.566(3)$ Å. The structure, solved by direct methods to a R value of 0.042 for 1131 reflections, consists of two independent 'half' molecules with the rhodium atoms in each having a square planar coordination.

Introduction

Reactions of symmetrical bidentate aldazines and ketazines with several transition metal ions have been the subject of many publications in the past [1, 2]. But there is no report in the literature on aromatic quadridentate azine derivatives of late Group VIII metals in their lower oxidation states. Preparation and thermal stability of salicylaldazinate metal complexes with Cu^{2+}, Ni^{2+} and Co^{2+} have been reported by Marvel and Bonsignore [3] and later their IR spectral studies have been carried out by Satpathy and Sahoo [4]. Boron and tin derivatives of symmetrical tetradentate azines have been reported by Tandon *et al.* [5, 6]; a tridentate coordination has been suggested in these complexes. As a continuation of our earlier publications on azines and mixed azine derivatives of titanium and tin organics [7, 8], we now report the synthesis and reactions of some azine derivatives of rhodium(I).

Experimental

Reactions were carried out in a dry, oxygen-free nitrogen atmosphere, using dried, freshly distilled and degassed solvents. The organic ligands used were of the highest purity available on the market. The azines and mixed azines were prepared as reported earlier [7–10]. $Rh_2(CO)_4Cl_2$ and $Rh(PPh_3)_3Cl$ were prepared by known methods [11, 12].

(a) Disodium Derivative of Salicylaldazine

Oil-free sodium hydride (0.048 g, 2 mmol) and salicylaldazine (0.240 g, 1 mmol) were mixed in ether (20 ml) and magnetically stirred for 3 h. Ether was then removed under reduced pressure and the solid was immediately suspended in benzene (20 ml).

(b) $[Rh(CO)_2]_2$(salicylaldazine)

The suspension of the sodium derivative of salicylaldazine in benzene [prepared in (a)] and $Rh_2(CO)_4Cl_2$ (0.388 g, 1 mmol) were mixed and refluxed for 3 h. The contents were then centrifuged to remove the insolubles and the clear benzene solution concentrated under reduced pressure. The orange solid obtained was washed with hexane and dried at 1 mm pressure. Yield 0.40 g (80%). Other derivatives of $Rh_2(CO)_4Cl_2$ (Table I) were obtained similarly.

(c) $[Rh(PPh_3)CO]_2$(salicylaldazine)

Triphenyl phosphine (0.576 g, 2.2 mmol) and $[Rh(CO)_2]_2$(salicylaldazine) (0.55 g, 1 mmol) were mixed in benzene (30 ml) and refluxed for 5 h. After cooling, the contents were centrifuged and the orange benzene solution was concentrated to crystallisation. It was washed with hexane many times and dried *in vacuo.* Yield 0.7 g (70%). Other derivatives of azines behaved similarly.

(d) $[Rh(COD)]_2$(salicylaldehyde-2-hydroxyacetophenoneazine)

1,5-Cyclooctadiene (0.059 g, 0.55 mmol) and $[Rh(CO)_2]_2$(Salacph) (0.142 g, 0.25 mmol) were

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TABLE 1. Binuclear Rhodium(I) Complexes of Aromatic Azines[a]

Compound	M.p. (°C)	Analysis (found (calc.) %)			
		C	H	N	P
(Sal-az)$Rh_2(CO)_4$ (1)	>230	38.90(38.84)	1.82(1.79)	4.80(5.03)	
(Brsal-az)$Rh_2(CO)_4$ (2)	>200	30.02(30.25)	1.01(1.12)	3.85(3.92)	
(Sal-az)$Rh_2(CO)_2(PPh_3)_2$ (3)	120	60.73(60.93)	3.84(3.90)	2.64(2.73)	6.62(6.05)
(Acph-az)$Rh_2(CO)_4$ (4)	>200	41.24(41.09)	2.18(2.39)	4.44(4.79)	
(Salba-az)$Rh_2(CO)_4$ (5)	>200	42.43(42.28)	2.17(2.34)	4.52(4.69)	
(Salacph-az)$Rh_2(CO)_4$ (6)	>200	40.12(40.00)	2.06(2.10)	4.65(4.91)	
(Salacph-az)Rh_2(COD) (7)	>200	55.55(55.19)	5.55(5.34)	4.71(4.15)	
(Sal-az)$Rh_2(PPh_3)_4$ (8)	110	69.47(69.17)	4.67(4.69)	1.76(1.87)	8.51(8.31)
(Salacph-az)$Rh_2(PPh_3)_4$ (9)	115	69.64(69.32)	4.55(4.78)	1.76(1.85)	8.88(8.23)

[a] Abbreviations: (Sal-az)H_2 = salicylaldazine, (Brsal-az)H_2 = 5-bromosalicylaldazine, (Acph-az)H_2 = 2-hydroxyacetophenone azine, (Salba-az)H_2 = salicylaldehyde benzoylacetone azine, (Salacph-az)H_2 = salicylaldehyde 2-hydroxyacetophenone azine, PPh_3 = triphenyl phosphine, COD = cyclooctadiene.

mixed in methanol (15 ml), refluxed for 3 h, cooled and the methanol solution was concentrated under reduced pressure to obtain a red solid. This was washed with hexane and dried at 1 mm pressure at room temperature. Yield 0.15 g, (90%).

(e) [Rh(PPh₃)₂]₂(salicylaldazine)

$Rh(PPh_3)_3Cl$ (1.84 g, 2 mmol) was added to a suspension of sodium derivative of salicylaldazine (1 mmol) prepared as in (a). The mixture was refluxed for 20 h and processed as in (b). Yield 0.9 g, (65%).

(f) Oxidative Bromination of 5-Bromosalicylaldazinotetracarbonyldirhodium

A suspension of 5-bromosalicylaldazinotetracarbonyldirhodium (0.7 g, 1 mmol) in methylene chloride (40 ml) was mixed with bromine (0.35 g, 2.2 mmol) in the same solvent. The mixture was allowed to react for 2 h under magnetic stirring after which the solvent was evaporated at reduced pressure. The dark coloured complex was washed with hexane and dried at 1 mm pressure. Yield 0.77 g (80%). The substance decomposes above 200 °C on heating. *Anal.* Found: C, 19.72; H, 0.63; Br (ionisable), 29.86. Calcd. for $C_{18}H_8O_6N_2Br_6Rh_2$: C, 20.89; H, 0.77; Br, 30.95%.

(g) X-ray Studies

Single crystals of salicylaldazinotetracarbonyldirhodium, suitable for X-ray work, were grown by recrystallisation of the complex from benzene. The specimens used had approximate dimensions of 0.05 × 0.125 × 0.6 mm. The formula weight 556.1; orthorhombic, *Pbnn*; $a = 10.480(2)$, $b = 15.831(2)$ and $c = 22.566(3)$ Å; density (by flotation) = 1.98 g/cm^3 (calc. = 1.97 g/cm^3); $Z = 8$.

The intensity data were collected on an Enraf-Nonius CAD4F 11M diffractometer using $\omega/2\theta$ scan technique with Mo Kα ($\lambda = 0.7107$ Å graphite monochromated) radiation. Cell dimensions were from 20 reflections ($14° \leqslant 2\theta \leqslant 32°$). 2752 reflections ($\theta \leqslant 23.5°$) were collected with three standard reflections measured every 1000 seconds. The variations in these standard reflections were within 2.5%. 1131 reflections with $|F_o| \geqslant 3\sigma|F_c|$ were used in the final refinement of structural parameters.

The structure was solved by direct methods using MULTAN-78 [13]. Full matrix least-squares refinement [14] of scale, positional and anisotropic thermal parameters of non-hydrogen atoms with stereochemically fixed hydrogens (isotropic thermal parameters) converged to an R of 0.042. A final Fourier difference map was featureless. Atomic scattering factors used were from the International Tables for X-ray crystallography [15]. Lists of observed and calculated structure factors and anisotropic thermal parameters are available from the Editor-in-Chief.

Results and Discussion

Reaction of the dimer $[Rh(CO)_2Cl]_2$ with stoichiometric amount of disodium derivative of 2-hydroxyaldazines and ketazines in refluxing benzene gave stable complexes of rhodium(I) having 2:1 metal to ligand formulation:

$$[Rh(CO)_2Cl]_2 + Na_2(\text{azine}) \longrightarrow [Rh(CO)_2]_2(\text{azine}) + 2NaCl$$

Symmetrical azines such as salicylaldazine, 5-bromosalicylaldazine and 2-hydroxyacetophenenone azine, and mixed azines like salicylaldehyde-benzoylacetone azine and salicylaldehyde-2-hydroxyacetophenone azine have been used for this study. The complexes are high melting, yellow to orange solids. The binuclear nature of the complexes has been confirmed from elemental analysis (Table I), molecular weight

TABLE II. IR (ν in cm^{-1}) and ^1H NMR (Chemical Shift in δ ppm) Spectral Data for the new Rhodium(I) Complexes

Compound[a]	ν(C=O)	ν(C=N)	ν(C−O)	ν(N−N)	$\delta(CH_3)$	γ(CH)	Aromatic protons	Aldehydic CH
1	2090, 2010	1605	1325	940			6.60–7.75	8.71
2	2100, 2030	1610	1320	965				
3	1970	1605	1325	925, 915			6.25–8.00	8.65, 8.75
4	2090, 2010	1605	1345	985	2.50, 2.70		6.60–7.80	
5	2080, 2020, 2000		1330	990, 975, 930	2.40	5.84	6.48–8.04	8.10
6	2090, 2030	1610	1325	925	2.70		6.60–7.80	8.31
7		1600	1325	920				8.45
8		1605	1315	920, 910				8.70
9		1595	1310	915				

[a] Compound labels same as in Table I.

and X-ray crystallographic data. These complexes did not react with molecular oxygen or liquid sulphur dioxide. However, both the rhodium atoms in the complex reacted with bromine in methylene chloride to give an octahedral rhodium(III) derivative:

$$[Rh(CO)_2]_2(\text{azine}) + 2Br_2 \longrightarrow [Rh(CO)_2Br_2]_2(\text{azine})$$

The carbonyl ligand substitution reaction in these rhodium(I) complexes has been carried out using a six-fold excess of triphenylphosphine in boiling benzene. Only monosubstituted products, $[RhCO(PPh_3)]_2$(azine), could be obtained in all the cases. However, 1,5-cyclooctadiene replaced both the carbonyls under similar reaction conditions.

The reaction of $Rh(PPh_3)_3Cl$ with disodium derivative of azines in 2:1 molar ratio has resulted in the isolation of bis(triphenylphosphine) derivative:

$$2Rh(PPh_3)_3Cl + Na_2(\text{azine}) \longrightarrow [Rh(PPh_3)_2]_2(\text{azine}) + 2NaCl$$

The phosphine ligands in these complexes could not be replaced by bubbling carbon monoxide through a boiling solvent medium.

IR Spectra

The IR spectra of the binuclear rhodium complexes of azines (Table II) show complete absence of hydrogen bonded hydroxyl stretching bands. The hydroxyl deformation modes found in the spectrum of salicylaldazine at 1310 cm^{-1} are also absent in the complexes. The complexes $[Rh(CO)_2]_2$(azine) exhibit two strong bands ~2090 and 2010 cm^{-1} due to terminal carbonyl stretching vibrations which suggest *cis* disposition of carbonyl groups about rhodium. The monocarbonyl derivatives, $[RhCO(PPh_3)]_2$(azine), show a single band at 1970 cm^{-1}. The ν(CN) at 1620 cm^{-1} in salicylaldazine is shifted to 1605 cm^{-1} in the complex indicating coordination of nitrogen lone pair to rhodium. There appears no splitting of ν(CN) due to dissimilar ring formation. The phenolic ν(CO) observed in the azine ligand 1275 cm^{-1} is shifted to 1320 cm^{-1} in the complexes as a result of proton replacement. An absorption at 900 cm^{-1} indicates N–N stretching in salicylaldazine. In the rhodium complex a high frequency shift to 940 cm^{-1} has been observed due to chelate formation. Similar shifts occur in the case of other complexes.

In the far IR region a medium band is seen at 500 cm^{-1} due to Rh–C stretching vibration [16, 17].

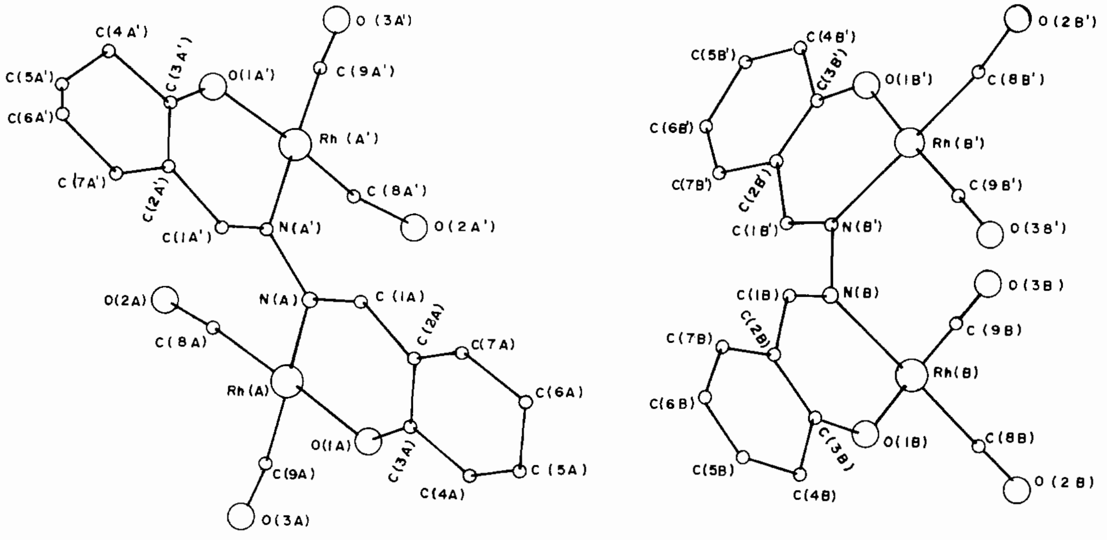
NMR Spectra

The ^1H NMR spectrum of $[Rh(CO)_2]_2$(salicylaldazine) shows CH=N resonance at ~δ 8.5 ppm, split symmetrically by 2 Hz. This could possibly be due to ^{103}Rh–H coupling. Similar feature is observed in the spectra of mixed azine complexes (Table II). An upfield shift of ~δ 0.2 is observed for the azomethine proton resonance in the complexes compared to those in free ligands due to anisotropic effect of carbonyl ligands. In acetophenone complexes a downfield shift of methyl protons is observed as expected.

Crystal Structure of Salicylaldazinotetracarbonyldirhodium

A perspective view of $C_{18}H_{10}N_2O_6Rh_2$ molecule is given in Fig. 1. The final positional and equivalent temperature factor for all non-hydrogen atoms are given in Table III. Table IV contains interatomic bond distances and angles along with e.s.d.s in parenthesis.

There are two independent 'half' molecules in the asymmetric unit. The centre of molecule **A** is on a two-fold axis parallel to the *a* axis while the centre of molecule **B** is on a two-fold axis parallel to the *b* axis. The two halves of both molecules are nearly perpendicular to each other (see Table V). Both molecules have similar conformation. The Rh–C bonds *trans* to the nitrogen atom of the chelate ring, is slightly longer (about 2 to 3 times the standard deviation) than the Rh–C bond *trans* to the oxygen atom in both molecules, indicating that the nitrogen atom has a larger *trans* influence than the oxygen atom. This is in agreement with the results for other chelate rings



(a) (b)

Fig. 1. Molecule A viewed along the *a* axis (a); molecule B viewed along the *a* axis (b).

TABLE III. Atomic Parameters with e.s.d.s in Parenthesis and Equivalent Isotropic Temperature Factors for non-H Atoms

Atom	x	y	z	B_{eq} (Å)^2
Rh(A)	0.0207(1)	0.2513(1)	0.0934(1)	4.39
O(1A)	0.0967(14)	0.1568(9)	0.1408(6)	4.68
O(2A)	−0.1111(21)	0.3888(14)	0.0312(9)	9.89
O(3A)	−0.1455(18)	0.2966(12)	0.1967(8)	7.82
N(A)	0.1460(15)	0.2237(9)	0.0264(6)	3.80
C(1A)	0.2357(20)	0.1693(12)	0.0268(8)	4.08
C(2A)	0.2589(19)	0.1092(12)	0.0746(8)	3.43
C(3A)	0.1879(23)	0.1075(16)	0.1267(10)	5.46
C(4A)	0.2203(20)	0.0411(13)	0.1668(9)	4.55
C(5A)	0.3185(24)	−0.0151(15)	0.1568(11)	5.95
C(6A)	0.3904(23)	−0.0128(16)	0.1027(11)	5.93
C(7A)	0.3580(24)	0.0511(17)	0.0663(11)	5.92
C(8A)	−0.0572(26)	0.3342(18)	0.0545(11)	5.70
C(9A)	−0.0867(25)	0.2777(16)	0.1553(11)	5.54
Rh(B)	0.2386(2)	0.3778(1)	0.1583(1)	4.84
O(1B)	0.3774(24)	0.3288(12)	0.1090(7)	4.98
O(2B)	0.1732(19)	0.5011(10)	0.0660(7)	4.96
O(3B)	0.0462(16)	0.4663(11)	0.2304(6)	10.15
N(B)	0.2879(12)	0.2930(8)	0.2220(4)	3.55
C(1B)	0.3772(15)	0.2371(11)	0.2206(6)	3.83
C(2B)	0.4636(16)	0.2252(11)	0.1729(7)	4.46
C(3B)	0.4622(18)	0.2717(12)	0.1227(7)	4.96
C(4B)	0.5627(18)	0.2528(15)	0.0811(7)	5.93
C(5B)	0.6514(21)	0.1909(15)	0.0912(10)	7.64
C(6B)	0.6506(21)	0.1478(16)	0.1445(9)	8.30
C(7B)	0.5568(20)	0.1644(13)	0.1817(9)	6.27
C(8B)	0.2010(24)	0.4520(13)	0.0999(8)	7.73
C(9B)	0.1202(20)	0.4285(12)	0.1994(9)	6.22

containing a nitrogen and an oxygen donor atom [18, 19]. The ring formed by the azomethine group, phenolic oxygen and rhodium is planar. The coordination around the rhodium atom in each molecule is square planar. The Rh–C≡O moiety is approximately linear average Rh–C≡O angle is 176(2)°. Such linear Rh–C≡O moiety has been observed in several structures [20]. The crystal structure is mainly stabilized by Van der Waal's interactions.

TABLE IV. Interatomic Bond Lengths (Å) and Bond Angles (°) with e.s.d.s in Parenthesis

Bond lengths	
O(1A)–C(3A)	1.27(3)
O(1A)–Rh(A)	2.00(1)
O(2A)–C(8A)	1.16(4)
O(3A)–C(9A)	1.16(3)
N(A)–C(1A)	1.27(3)
N(A)–Rh(A)	2.05(1)
C(1A)–C(2A)	1.46(3)
C(2A)–C(3A)	1.39(3)
C(2A)–C(7A)	1.40(3)
C(3A)–C(4A)	1.43(3)
C(4A)–C(5A)	1.38(3)
C(5A)–C(6A)	1.44(4)
C(6A)–C(7A)	1.35(4)
C(8A)–Rh(A)	1.78(3)
C(9A)–Rh(A)	1.84(3)
O(1B)–C(3B)	1.31(3)
O(1B)–Rh(B)	1.99(2)
O(2B)–C(8B)	1.13(3)
O(3B)–C(9B)	1.20(3)
N(B)–C(1B)	1.29(2)
N(B)–Rh(B)	2.03(1)
C(1B)–C(2B)	1.42(2)
C(2B)–C(3B)	1.35(2)
C(2B)–C(7B)	1.39(3)
C(3B)–C(4B)	1.44(3)
C(4B)–C(5B)	1.37(3)
C(5B)–C(6B)	1.38(3)
C(6B)–C(7B)	1.32(3)
C(8B)–Rh(B)	1.81(2)
C(9B)–Rh(B)	1.74(2)
N(A)–N(A′)	1.45(2)
N(B)–N(B′)	1.49(1)
Bond angles	
C(3A)–O(1A)–Rh(A)	128(1)
C(1A)–N(A)–Rh(A)	128(1)
N(A)–C(1A)–C(2A)	125(2)
C(1A)–C(2A)–C(3A)	123(2)
C(1A)–C(2A)–C(7A)	117(2)
C(3A)–C(2A)–C(7A)	120(2)
O(1A)–C(3A)–C(2A)	127(2)
O(1A)–C(3A)–C(4A)	118(2)
C(2A)–C(3A)–C(4A)	115(2)
C(3A)–C(4A)–C(5A)	123(2)
C(4A)–C(5A)–C(6A)	121(2)
C(5A)–C(6A)–C(7A)	114(2)
C(2A)–C(7A)–C(6A)	127(2)
O(2A)–C(8A)–Rh(A)	177(2)
O(3A)–C(9A)–Rh(A)	174(2)
C(3B)–O(1B)–Rh(B)	129(2)
C(1B)–N(B)–Rh(B)	128(1)
N(B)–C(1B)–C(2B)	125(1)
C(1B)–C(2B)–C(3B)	124(2)
C(1B)–C(2B)–C(7B)	116(2)
C(3B)–C(2B)–C(7B)	120(2)
O(1B)–C(3B)–C(2B)	126(2)
O(1B)–C(3B)–C(4B)	119(2)
C(2B)–C(3B)–C(4B)	115(2)
C(3B)–C(4B)–C(5B)	122(2)
C(4B)–C(5B)–C(6B)	120(2)
C(5B)–C(6B)–C(7B)	117(2)
C(2B)–C(7B)–C(6B)	125(2)
O(2B)–C(8B)–Rh(B)	176(2)
O(3B)–C(9B)–Rh(B)	175(2)
O(1A)–Rh(A)–N(A)	89(1)
O(1A)–Rh(A)–C(8A)	176(1)
O(1A)–Rh(A)–C(9A)	90(1)
N(A)–Rh(A)–C(8A)	95(1)
N(A)–Rh(A)–C(9A)	178(1)
C(8A)–Rh(A)–C(9A)	86(1)
O(1B)–Rh(B)–N(B)	87(1)
O(1B)–Rh(B)–C(8B)	90(1)
O(1B)–Rh(B)–C(9B)	176(1)
N(B)–Rh(B)–C(8B)	177(1)
N(B)–Rh(B)–C(9B)	96(1)
C(8B)–Rh(B)–C(9B)	86(1)
C(1A)–N(A)–N(A′)	113(1)
Rh(A)–N(A)–N(A′)	119(1)
Rh(B)–N(B)–N(B′)	118(1)
N(B)–N(B′)–C(1B′)	114(1)

TABLE V. Some Important Torsional Angles (°)

Rh(A)–O(1A)–C(3A)–C(2A)	2
O(1A)–C(3A)–C(2A)–C(1A)	−1
C(3A)–C(2A)–C(1A)–N(A)	−3
C(2A)–C(1A)–N(A)–Rh(A)	6
C(1A)–N(A)–Rh(A)–O(1A)	−5
N(A)–Rh(A)–O(1A)–C(3A)	1
Rh(B)–O(1B)–C(3B)–C(2B)	9
O(1B)–C(3B)–C(2B)–C(1B)	−5
C(3B)–C(2B)–C(1B)–N(B)	0
C(2B)–C(1B)–N(B)–Rh(B)	2
C(1B)–N(B)–Rh(B)–O(1B)	1
N(B)–Rh(B)–O(1B)–C(3B)	−6
Rh(A)–N(A)–N(A′)–Rh(A′)	−86
Rh(B)–N(B)–N(B′)–Rh(B′)	−84

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