

Polyhedron 18 (1999) 1135-1140



# New hydrogen-bonded dimeric and polymeric gold(I) complexes of the heterodifunctional ligand Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub>

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Received 1 October 1998; accepted 3 November 1998

# Abstract

The preparation of several new gold(I) complexes by chloride metathesis of [AuCl(**HL**)] [**HL**=Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub>] with either **HL** or K[Ph<sub>2</sub>P(E)NP(E)Ph<sub>2</sub>] (E=S or Se) is described. All compounds were characterised by a combination of <sup>31</sup>P{<sup>1</sup>H}, <sup>1</sup>H and IR spectroscopy, microanalysis and X-ray crystallography. X-ray structural studies reveal that [Au(**HL**)<sub>2</sub>]Cl [monoclinic, space group  $P2_1/c$ , a=9.0726(3) Å, b=21.0847(6) Å, c=12.0131(3) Å,  $\beta=105.1090(10)^\circ$ , V=2219 Å<sup>3</sup>, Z=2, final R=3.97] forms a one dimensional polymeric structure in which alternating [Au(**HL**)<sub>2</sub>]<sup>+</sup> and Cl<sup>-</sup> ions are linked through intermolecular N–H···Cl hydrogen-bonding. In contrast the three-co-ordinate compound [Au{Ph<sub>2</sub>P(Se)NP(Se)Ph<sub>2</sub>-Se,Se '}(**HL**)] [monoclinic, space group  $P2_1/a$ , a=21.6752(5) Å, b=9.1200(10) Å, c=24.0742(7) Å,  $\beta=106.080(2)^\circ$ , V=4573 Å<sup>3</sup>, Z=4, final R=8.94] forms hydrogen-bonded dimer pairs analogous to that previously observed in non-complexed **HL**. The X-ray crystal structure of the gold(I) precursor [AuCl(**HL**)] has also been determined: monoclinic, space group  $P2_1/c$ , a=10.217(8) Å, b=23.256(5) Å, c=20.086(5) Å,  $\beta=101.15(4)^\circ$ , V=4683 Å<sup>3</sup>, Z=8, final R=5.2. The X-ray crystal structure reveals intermolecular N–H···O=P hydrogen-bonding between adjacent [AuCl(**HL**)] molecules forming infinite chains. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Gold(I) complexes; Chloride metathesis; X-ray crystallography; Heterodifunctional ligands

## 1. Introduction

Gold(I) coordination complexes with stabilising tertiary phosphines have been extensively studied [1,2] partly due to their biological importance especially in the treatment of rheumatoid arthritis. Our interests pertain to the development of new heterodifunctional ligands that incorporate both a "soft" [e.g. P(III)] and "hard" (e.g. O, N) donor centre. These hybrids are particularly attractive since the "soft" donor centre is an excellent platform for ligating low-valent late transition metals, yet complexation studies of these ligands toward gold(I) has been poorly exploited. We recently described the synthesis, complexation and monochalcogenide reactivity studies of the  $Ph_2PNHP(O)Ph_2$  (hereafter abbreviated HL) and the asymmetrical anions  $[Ph_2P(E)NP(O)Ph_2]^-$  (E=S or Se) [3-8]. One reoccurring theme through much of the metal chemistry of HL is the persistence of hydrogen-bonding with several different motifs verified by X-ray crystallographic studies. Thus in the noncomplexed ligand HL, two

molecules are N-H...OP hydrogen-bonded forming a dimer pair [3] (type I), akin to that previously seen in the bischalcogenides  $Ph_2P(E)NHP(E)Ph_2$  (E=S or Se) [9–12]. The amine proton of a coordinated HL can also forge strong intramolecular N-H···X (X=Cl, Br) hydrogenbonds with other auxiliary ligands (type II) as exemplified by the square-planar complexes cis-[PtBr<sub>2</sub>(**HL**)<sub>2</sub>], trans-[Pt(CH<sub>3</sub>)Cl(HL)<sub>2</sub>] and [RhCl(cod)(HL)] (cod=cyclo-octa-1,5-diene) [3,4]. In contrast, the cations  $[Pd(\eta^3 C_{3}H_{5}$ )(**HL**)][BF<sub>4</sub>] and [Pt(**HL**)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (**HL**=neutral P,O-chelate) display intermolecular bifurcated H-bonding interactions (type III) of the NH group of HL with a tetrafluoroborate anion (type III) [3,6]. Quaternisation of the phosphorus(III) centre of HL with CH<sub>3</sub>I gave the phosphonium salt [{Ph<sub>2</sub>P(CH<sub>3</sub>)NP(O)Ph<sub>2</sub>}<sub>2</sub>H]I containing a linear O···H···O hydrogen-bond [5]. Hydrogen-bonding arrangements such as type IV and V have not, to the best of our knowledge, been previously described with the neutral HL ligand although in a recently reported cobalt complex the deprotonated anion [Ph<sub>2</sub>PNP(O)Ph<sub>2</sub>]<sup>-</sup> displays an O-H...OP intermolecular hydrogen-bond with a  $CH_3OH$  solvate [13]. Here we demonstrate the effect of a linear and trigonal planar metal centre on hydrogen-bond-

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ing possibilities. The synthesis and characterisation of [AuCl(HL)],  $[Au(HL)_2]X$  (X=Cl, PF<sub>6</sub>) and the three-coordinate complexes  $[Au\{Ph_2P(E)NP(E)Ph_2-E,E'\}(HL)]$ (E=S or Se) are reported. X-ray studies on representative examples reveal some new patterns of hydrogen-bonding (types IV and V).



# 2. Experimental

#### 2.1. General

The ligands  $Ph_2PNHP(O)Ph_2$  (**HL**) and  $[Ph_2P(E)NP(E)Ph_2]^-$  (E=S or Se) were prepared according to a literature method [3,12,14] as were [AuCl(tht)] (tht=tetrahydrothiophene) and [AuCl(**HL**)] **1** [4,15]. Crystals of **1** suitable for X-ray crystallography were grown by slow diffusion of diethyl ether into a  $CDCl_3/CH_3OH$  solution of [AuCl(tht)]/**HL** (1:1 molar ratio) over the course of ca. 7 days.

Infrared spectra were recorded on KBr discs in the range 4000–200 cm<sup>-1</sup> on a Perkin-Elmer System 2000 FT-IR spectrometer. <sup>1</sup>H NMR spectra (250 MHz) were recorded on a Bruker AC250 FT NMR spectrometer with  $\delta$  referenced to external TMS. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra (36.2 MHz) were recorded on a Jeol FX90Q spectrometer with  $\delta$  referenced to external phosphoric acid. Elemental analyses (Perkin-Elmer 2400 CHN Elemental Analyzer) were performed by the Loughborough University Service within the Department of Chemistry.

# 2.2. Preparations

2.2.1. Preparation of  $[Au\{Ph_2PNHP(O)Ph_2-P\}_2]Cl$ , **2a** To the solids [AuCl(tht)] (0.012 g, 0.0374 mmol) and

Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub> (0.030 g, 0.0747 mmol) was added CDCl<sub>3</sub> (ca. 0.5 cm<sup>3</sup>) and several drops of CH<sub>3</sub>OH. The solution was monitored immediately by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and showed that **2a** was the only phosphorus containing species present. Slow diffusion of diethyl ether into the CDCl<sub>3</sub>/CH<sub>3</sub>OH solution of **2a** over the course of ca. 7 days gave crystals suitable for X-ray crystallography. Yield: 0.029 g, 75%. Anal. Calcd (found) for C<sub>48</sub>H<sub>42</sub>N<sub>2</sub>P<sub>4</sub>O<sub>2</sub>AuCl: C, 55.70 (54.90); H, 4.10 (3.90); N, 2.70 (2.35).

# 2.2.2. Preparation of $[Au\{Ph_2PNHP(O)Ph_2-P\}_2]PF_6$ , **2b**

To the solids [AuCl(tht)] (0.049 g, 0.153 mmol) and  $Ph_2PNHP(O)Ph_2$  (0.126 g, 0.314 mmol) was added  $CH_3OH$  (1 cm<sup>3</sup>). The clear solution was stirred for ca. 5 min and  $[NH_4][PF_6]$  (0.061 g, 0.374 mmol) in  $CH_3OH$  (minimum volume) added. After stirring for an additional 5 min, distilled water was added dropwise to give a white precipitate **2b**. The solid was collected by suction filtration and dried in vacuo. Yield: 0.158 g, 90%. Anal. Calcd (found) for  $C_{48}H_{42}N_2P_5O_2AuF_6.2H_2O$ : C, 48.80 (48.65); H, 3.95 (3.50); N, 2.35 (2.00).

# 2.2.3. Preparation of [Au{Ph<sub>2</sub>P(Se)NP(Se)Ph<sub>2</sub>-Se,Se'}-{Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub>-P}], **3**

A suspension of  $[AuCl{Ph_2PNHP(O)Ph_2-P}]$  (0.056 g, 0.0884 mmol) in CH<sub>3</sub>OH (1 cm<sup>3</sup>) was treated with K[Ph<sub>2</sub>P(Se)NP(Se)Ph<sub>2</sub>] (0.054 g, 0.0929 mmol). After stirring the suspension for ca. 20 min the product was collected by suction filtration and dried in vacuo. Yield: 0.087 Anal. Calcd (found) g, 86%. for C48H41N2P4OSe2Au: C, 50.55 (50.05); H, 3.65 (3.50); N, 2.45 (2.10). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.90–7.15 (arom. H), 5.46 (NH). Slow diffusion of CH<sub>3</sub>OH into a CDCl<sub>3</sub> solution of 3 over the course of several weeks gave crystals suitable for X-ray crystallography.

In a similar manner  $[Au{Ph_2P(S)NP(S)Ph_2-S,S'}{Ph_2PNHP(O)Ph_2-P}]$  **4** was prepared (88%). Anal. Calcd (found) for  $C_{48}H_{41}N_2P_4OS_2Au1.5CH_3OH: C, 54.30$  (53.75); H, 4.35 (4.15); N, 2.55 (2.60). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.96–7.20 (arom. H), 6.75 (NH).

#### 2.3. X-ray crystallography

Details of crystal data collections and refinements are given in Table 1. X-ray diffraction measurements were made with graphite-monochromated Mo-K<sub> $\alpha$ </sub> radiation ( $\lambda$ = 0.710 73 Å) using a Siemens SMART diffractometer (**2a** and **3**), or with Cu-K<sub> $\alpha$ </sub> radiation ( $\lambda$ =1.541 78 Å) and a Rigaku AFC7S serial diffractometer (**1**). For the SMART data, intensities were collected using 0.3° or 0.15° width  $\omega$ steps accumulating area detector frames spanning a hemisphere of reciprocal space for all structures (data were integrated using the SAINT [16] program) and for the Rigaku AFC7S data collections by  $\omega$  scans over a single Crystallographic data for [AuCl{Ph,PNHP(O)Ph,-P}] 1, [Au{Ph,PNHP(O)Ph,-P},]Cl 2a and [Au{Ph,P(Se)NP(Se)Ph,-Se,Se'}{Ph,PNHP(O)Ph,-P}] 3

Compound	1	2a	3	
Empirical formula	$C_{24}H_{21}AuClNOP_2$	$C_{48}H_{42}AuClN_2O_2P_4$	$C_{48}H_{41}AuN_2OP_4Se_2$	
Space group	$P2_1/c$	$P2_1/c$	$P2_1/a$	
Unit cell dimensions				
a (Å)	10.217(8)	9.0726(3)	21.6752(5)	
b (Å)	23.256(5)	21.0847(6)	9.1200(10)	
c (Å)	20.086(5)	12.0131(3)	24.0742(7)	
$\beta$ (deg)	101.15(4)	105.1090(10)	106.080(2)	
Volume (Å <sup>3</sup> )	4683	2219	4573	
Z value	8	2	4	
Formula weight	633.80	1035.13	1140.59	
final R	5.2	3.97	8.94 <sup>a</sup>	

<sup>a</sup> Poor crystal quality.

quadrant of reciprocal space. All data were corrected for Lorentz-polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections or by empirical methods.

Structures were solved by direct methods and refined by full-matrix least-squares against F (teXsan) or  $F^2$ (SHELXTL) for all data with  $I > 2\sigma(I)$  with weights, w, set equal to  $[\sigma_{c}^{2}(F_{0}^{2})+(aP)^{2}+bP]^{-1}$ , where  $P = [\max(F_{0}^{2},0)+$  $2F_{c}^{2}$ ]/3 parameter, x, of the form  $k[1+0.001 \ x \ F_{c}^{2}]^{3}$ / sin(2q)<sup>0.25</sup> was refined for the SMART/SHELXTL [17] structures: the weighting scheme for the Rigaku/TEXSAN [18] was as previously reported [7]. The carbon atoms in the structure of 3 were refined isotropically because of a poor data/parameter ratio, all other non hydrogen atoms were refined anisotropically. The N-H proton in 2a was allowed to refine freely. All other hydrogen atoms were assigned isotropic displacement parameters and were constrained to idealised geometries. Refinements converged to residuals given in Table 1. All calculations were made with programs of SHELXTL or TEXSAN systems.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 103145 (for 1), 103146 (for 2a) and 103147 (for 3). Copies of the data can be obtained, free of

Table 2					
Selected	spectroscopic	data	for	complexes	1 - 4

charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, (fax +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

# 3. Results and discussion

Reaction of Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub> (HL) with [AuCl(tht)] (tht=tetrahydrothiophene) in a 1:1 molar ratio has previously been shown to give the linear gold(I) compound [AuCl(HL)] 1 in high yield [4]. We now find that treatment of [AuCl(tht)] with HL in a 1:2 molar ratio proceeds smoothly to afford the homoleptic complex [Au(HL)<sub>2</sub>]Cl 2a as the chloride salt. Alternatively treatment of 1 with one equivalent of HL leads to chloride displacement and the formation of 2a (<sup>31</sup>P{<sup>1</sup>H} NMR evidence). Chloride metathesis of 2a with  $[NH_4][PF_6]$  in methanol gave the hexafluorophosphate salt 2b. The spectroscopic and microanalytical data for the cations 2a, b (Table 2 and Section 2) are in full accord with the proposed structures. Particularly diagnostic is the <sup>31</sup>P{<sup>1</sup>H} NMR spectra which show two singlet resonances [J(PP) not resolved] for the coordinated P(III) and "dangling" P(O) centres with  $\delta(P_O)$ for 2a, b (26.8 and 27.1 ppm respectively) similar to that reported for 1 (26.4 ppm) [4]. Furthermore the absence of

Compound	$\delta(P)$	$\delta(P_{O})$	J(PP)	$\delta(P_E)^a$	J(PSe)	<i>ν</i> (PO)	$\nu(\text{PE})^{a}$
1	53.9	26.4	n.r.			1184 <sup>b</sup>	
2a	64.7	26.8	n.r.			1204	
2 <b>b</b> <sup>c,d</sup>	65.0	27.1	n.r.			1196	
3	67.4	23.5	26.4	26.2	567	1231, 1209,	538
						1187, 1180 <sup>e</sup>	
4	63.8	24.1	28.6	36.1		1214, 1199, 1176 <sup>e</sup>	556

n.r.=not resolved.

<sup>a</sup> E = S or Se.

<sup>b</sup> Taken from Ref. [2].

<sup>c</sup> Measured in CDCl<sub>3</sub>/CH<sub>3</sub>OH.

<sup>d</sup>  $PF_6^-$  anion also detected.

<sup>e</sup> In addition to  $\nu_{asym}(P_2N)$  absorptions.



Fig. 1. Crystal structure of [AuCl{Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub>-P}], 1.

 $\nu$ (AuCl) absorptions in the IR spectra of **2a**, **b** is consistent with  $[L-Au-L]^+$  cation formation. Interestingly the only other example of a gold complex with **HL** is *cis*-[Au-(CH<sub>3</sub>)<sub>2</sub>Cl(**HL**)] isolated from aerial oxidation of the noncoordinated P(III) centre in *cis*-[Au-(CH<sub>3</sub>)<sub>2</sub>Cl{Ph<sub>2</sub>PNHPPh<sub>2</sub>-*P*}] [19].

Coordination complexes of  $[Ph_2P(E)NP(E)Ph_2]^-$  (E= O, S or Se) are well known for numerous metal ions and readily accessible, in most instances, by simple transmetallation reactions. Surprisingly gold compounds of  $[Ph_2P(E)NP(E)Ph_2]^-$ , in which both E donor atoms are identical, are relatively uncommon [20–22]. Furthermore we recently described a new *E*-monodentate coordination mode for the unsymmetrical ligands  $[Ph_2P(O)NP(E)Ph_2]^-$ (E=S or Se) at a d<sup>10</sup> gold centre [8]. In contrast copper chemistry with these ligands is often unpredictable and has been shown to give either mononuclear or multimetallic species depending upon the choice of starting material [23]. When **1** is allowed to react at room temperature with one equivalent of K[Ph<sub>2</sub>P(E)NP(E)Ph<sub>2</sub>] (E=S or Se) in CH<sub>3</sub>OH the mixed three-co-ordinate complexes [Au{Ph<sub>2</sub>P(E)NP(E)Ph<sub>2</sub>-*E*,*E'*}(**HL**)] (E=Se **3**; E=S **4**) were isolated in high yields (>85%). The neutral compound **4** was independently synthesised from **2b** and one equivalent of K[Ph<sub>2</sub>P(S)NP(S)Ph<sub>2</sub>]. The spectroscopic data are given in Table 2 and are unexceptional.

The X-ray crystal structures of 1, 2a and 3 (Figs. 1–4, Table 3) have been determined. To our knowledge 3 is the first crystallographically characterised gold(I) complex of  $[R_2P(E)NP(E)R_2]^{-}$ . Both 1 and 2a display a two-coordinate linear geometry [P(2)-Au(1)-Cl(1) 174.2(2), P(4)-Au(2)-Cl(2) 174.8(3)° for 1 (two independent molecules)]; P(2)-Au(1)-P(2A) 180° for 2a]. In contrast compound  $\mathbf{3}$  is three-co-ordinate with the gold centre 0.17 Å out of the plane of the three substituents. The Au-P bond lengths in all three examples are different as a consequence of the trans ligand [Au(1)-P(2) 2.224(7) and Au(2)-P(4) 2.229(6) Å for 1; Au(1)-P(2) 2.332(2) for 2a;Au(1)-P(2) 2.286(4) Å for 3]. The six-membered ring geometry in the three-co-ordinate complex 3 (Fig. 4) is best described as pseudo-boat with Se(3) and P(4) at the stern and prow positions. The P(4)-N(3)-P(3)-Se(3) mean plane [maximum deviation 0.23 Å for N(3)] is hinged by  $47^{\circ}$  with respect to the Au(1)-Se(3)-P(4)-Se(4) mean plane [maximum deviation 0.09 Å for Se(4)]. The monodentate Ph2PNHP(O)Ph2 ligand in the twocoordinate complexes have the P=O oxygen atoms anti to the N–H groups and syn to the Au centres with Au···O distances of 3.26 and 3.20 Å [Au(1) $\cdots$ O(1) and Au(2) $\cdots$ O(3) respectively] for 1 and 3.14 Å [Au(1) $\cdots$ O(1)] for 2a. This is not possible in 3 because of dimer pair formation (Fig. 3) between N-H···O=P [N(1A)···O(1) 2.87 Å,  $H(1AA)\cdots O(1) 2.12 \text{ Å}, N(1A)-H(1AA)\cdots O(1) 144^{\circ}].$ 



Fig. 2. Crystal structure of [Au{Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub>-P}<sub>2</sub>]Cl, 2a.



Fig. 3. Crystal structure of [Au{Ph<sub>2</sub>P(Se)NP(Se)Ph<sub>2</sub>-Se,Se'}{Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub>-P}], **3**.

Compound **1** also displays hydrogen-bonding but in this case to form infinite chains (type IV). Within the asymmetric unit the two independent molecules are linked via N–H···O bonds [N(1)···O(3) 2.89 Å, H(1n)···O(3) 2.11 Å, N(1)–H(1n)···O(3) 138°]. Furthermore infinite molecules are linked through N(3\*)–H(3n\*)···O(1) hydrogenbonds [N(3\*)···O(1) 2.82 Å, H(3n\*)···O(1) 1.88 Å, N(3\*)–H(3n\*)···O(1) 168°]. The cationic complex **2a** forms one dimensional chains (type V) via N–H···Cl hydrogen-bonding [N(1)···Cl(1) 3.27 Å, H(1)···Cl(1) 2.43 Å, N(1)–H(1)···Cl 168°].

These three structures illustrate the potential of  $Ph_2PNHP(E)Ph_2$  ligands in the formation of a range of engineered hydrogen-bonded molecular solids. In **1** the

P=O appears to be a better hydrogen-bonding centre than Au–Cl. However in **2a** the Cl<sup>-</sup> provides a good H···Cl system and so this is preferred over N–H···O=P bonding to generate the polymeric material **2a**. These results illustrate the necessity for the N–H to find a hydrogenbonding acceptor site. Further work into the control of this architecture is underway.

## Acknowledgements

We should like to thank the EPSRC for support and the JERI for provision of an equipment grant.



Fig. 4. Core geometry of [Au{Ph<sub>2</sub>P(Se)NP(Se)Ph<sub>2</sub>-Se,Se'}{Ph<sub>2</sub>PNHP(O)Ph<sub>2</sub>-P}], 3.

Table 3 Selected bond lengths (Å) and angles (°) for compounds 1, 2a and 3

<b>1</b> <sup>a</sup>	2a	3
2.224(7) [2.229(6)]	2.332(2)	2.286(4)
1.652(18) [1.684(16)]	1.698(7)	1.67(2)
1.661(18) [1.657(18)]	1.668(7)	1.70(2)
1.508(14) [1.464(15)]	1.493(6)	1.51(2)
2.272(7) [2.264(6)]		
		2.597(3)
		2.565(2)
		2.182(5)
		1.61(2)
		1.61(2)
		2.184(5)
113.9(7) [110.3(7)]	111.1(3)	121.4(5)
123.7(11) [124.4(10)]	123.1(4)	132.8(11)
112.6(9) [113.1(10)]	114.5(4)	111.4(9)
174.2(2) [174.8(3)]		
		120.8(2)
		127.2(2)
		110.62(7)
		95.9(2)
		119.0(7)
		133.9(10)
		119.6(6)
		104.5(2)
	1 <sup>a</sup> 2.224(7) [2.229(6)]   1.652(18) [1.684(16)]   1.661(18) [1.657(18)]   1.508(14) [1.464(15)]   2.272(7) [2.264(6)]   113.9(7) [110.3(7)]   123.7(11) [124.4(10)]   112.6(9) [113.1(10)]   174.2(2) [174.8(3)]	1 <sup>a</sup> 2a     2.224(7) [2.229(6)]   2.332(2)     1.652(18) [1.684(16)]   1.698(7)     1.652(18) [1.657(18)]   1.668(7)     1.508(14) [1.464(15)]   1.493(6)     2.272(7) [2.264(6)]   2.272(7)     113.9(7) [110.3(7)]   111.1(3)     123.7(11) [124.4(10)]   123.1(4)     112.6(9) [113.1(10)]   114.5(4)     174.2(2) [174.8(3)]   114.5(4)

<sup>a</sup> Values in square brackets are the equivalent parameter in the second molecule.

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