Synthesis of Complexes $[Au(PPh_3)L]^+$ (L = Primary, Secondary or Tertiary Amine). Crystal Structure of $[Au(PPh_3)(NMe_3)][ClO_4]\cdot CH_2Cl_2^{\dagger}$

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The 1:1 reaction of $[Au(acac)(PPh_3)]$ (Hacac = acetylacetone) with ammonium salts [HL]X (X = CF₃SO₃, L = 2-nitroaniline, 4-methoxyaniline, NHPh₂ or NHEt₂; X = ClO₄, L = NMe₃) in diethyl ether gave complexes $[Au(PPh_3)L]X$ and acetylacetone. The crystal structure of $[Au(PPh_3)(NMe_3)][ClO_4]$ was determined; orthorhombic, space group $P2_12_12_1$, a = 9.498(2), b = 10.322(2), c = 26.154(4) Å, $wR(F^2)$ 0.091. The gold atom is linearly co-ordinated to both ligands [Au-P 2.231(2), Au-N 2.108(7) Å, P-Au-N 179.3(2)°] and no intermolecular Au • • Au contacts exist.

Gold(I) complexes with neutral N-donor ligands are much less common than those with P-donor ligands because of the soft acid nature of the metal centre. For instance, $[AuX(ER_3)]$ and $[Au(ER_3)_2]^+$ complexes with E = P are known for a wide range of X and R groups,¹ whereas, as far as we are aware, only one complex of each type with E = N has been reported, namely the rather unstable [AuCl(pip)] (pip = piperidine) and $[Au(pip)_2]^+$.² Therefore, mixed complexes $[Au(PR_3)(NR'_3)]^+$ might be expected to be of intermediate stability. However, only a few such complexes have been described with full experimental or spectroscopic details.³ Only one of them [Au(PPh₃)-(qncd)]BF₄ (qncd = quinuclidine)^{3d} has been characterized by X-ray diffraction methods. These complexes are prepared (usually in low yields) by the reaction of [AuX(PR₃)] with the corresponding amine, where X is ClO_4^- , BF_4^- or NO_3^- . We report in this paper a method to prepare some related mixedligand complexes and the crystal structure of one of them.

Results and Discussion

By reacting $[Au(acac)(PPh_3)]$ (Hacac = acetylacetone) with ammonium salts $[NHRR'_2]X$ (1:1), the cationic complexes $[Au(PPh_3)(NRR'_2)]X$ (X = ClO₄, R = R' = Me 1; X = CF₃SO₃, R = H, R' = Et 2; R = H, R' = Ph 3; R = C₆H₄-NO₂-2, R' = H4; R = C₆H₄OMe-4, R' = H 5) can be isolated [equation (1)]. Except for 4, all complexes were obtained in

 $[Au(acac)(PPh_3)] + [NHRR'_2]X \longrightarrow$ Hacac + [Au(PPh_3)(NRR'_2)]X (1)

high yield (78-95%).

The result of these reactions depends on the nature of the solvent. Thus, acetone could only be used in the case of the synthesis of the tertiary amine complex 1, while a mixture of complexes is obtained for primary and secondary amines. We

† Gold(1) Complexes with N-Donor Ligands. Part 1.

assume that complexes 2-5, behaving as ammonium salts, react rapidly in acetone with $[Au(acac)(PPh_3)]$ to give gold(1) complexes with bridging amido or imido ligands [equations (2)-(4)].

 $[Au(acac)(PPh_3)] + [Au(PPh_3)(NHR'_2)]X \longrightarrow \\ Hacac + [(AuPPh_3)_2(\mu - NR'_2)]X \quad (2)$

 $[Au(acac)(PPh_3)] + [Au(PPh_3)(NH_2R)]X \longrightarrow$ $Hacac + [(AuPPh_3)_2(\mu-NHR)]X \quad (3)$

 $[Au(acac)(PPh_3)] + [(AuPPh_3)_2(\mu-NHR)]X \longrightarrow$ Hacac + [(AuPPh_3)_3(\mu_3-NR)]X (4)

Examples of these aurioammonium salts, *i.e.* one diaurioammonium salt $[(AuPPh_3)_2(\mu-NHC_6H_4NO_2-4)]BF_4$,⁴ and several triaurioammonium salts $[(AuPPh_3)_3(\mu_3-NR)]BF_4$ (R = alkyl or aryl) have been described.^{4,5} The tendency of gold(1) to establish weak intramolecular Au···Au bonding interactions (aurophilicity)⁶ in these di- or tri-nuclear complexes is probably the reason why they are much more stable than complexes 1–5, which slowly decompose in the solid state and in solution. This is also likely to be the reason for the formation of the very stable $[(AuPPh_3)_4(\mu_4-N)]BF_4$ ⁷ and the hypervalent $[(AuPPh_3)_5(\mu_5-N)]BF_4$ ⁸ complexes. Although this stabilizing aurophilicity can also lead to intermolecular Au···Au interactions,⁶ these were not observed in the only previously reported crystal structure of a monoaurioammonium salt $[Au(PPh_3)(qncd)]BF_4$,^{3d} or in complex 1 (see below).

The success of reactions leading to complexes 2-4 relied on the use of diethyl ether because of the solubility of the ammonium trifluoromethanesulfonates and $[Au(acac)(PPh_3)]$ and the insolubility of the resulting complexes in this solvent. Probably, the rapid precipitation of complexes 2-4 allows the corresponding reactions to be performed without special precautions against atmospheric moisture and prevents reactions (2)-(4). In those reported methods where reaction conditions were indicated,^{3b-d} a dinitrogen atmosphere was used. Careful precautions to eliminate all traces of moisture from the reactants proved to be vital for the generation of $[Au(PPh_3)(qncd)]BF_4$.^{3d} In the presence of water, the reaction between quinuclidine and $[Au(PPh_3)]BF_4$ gives quinuclidinium and $[(AuPPh_3)_3O]^+$ salts.^{3d}

Supplementary data available: Full details have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlichtechnische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD 401358.



Scheme 1 (i) +[Au(acac)(PPh₃)] - Hacac; (ii) + 2[Au(acac)(PPh₃)] - 2 Hacac; (iii) + 3[Au(acac)L] (L = PPh₃) - 3 Hacac; (iv) +4 [Au(acac)L] (L = PMe₂Ph) - 4 Hacac; (v) + [Au(acac)₂]⁻ - 2 Hacac

This is a new example of the utility of acetylacetonatogold(1) complexes as starting materials for the synthesis of gold(1) complexes (see Scheme 1).⁹ We have previously used [Au(acac)(PPh₃)] to prepare mono-, di-, tri- and tetra-nuclear gold(1) complexes. More recently Laguna and co-workers¹⁰ have also found interesting synthetic applications for [Au(acac)(PPh₃)].

All complexes behave in solution as 1:1 electrolytes.¹¹ The IR spectra of complexes 2, 4 and 5 show v(NH) in the region 3214–3092 cm⁻¹. For complex 3, v(NH) could not be assigned because only very weak bands in this region were observed.

Structure of Complex 1.—The structure of complex 1 (see Fig. 1 and Table 1) consists of the cation $[Au(PPh_3)(NMe_3)]^+$, a perchlorate anion and a dichloromethane molecule. In the cation the gold atom is linearly co-ordinated $[P-Au-N 179.3(2)^\circ]$. The Au–N and Au–P bond distances [2.108(7) and 2.231(2) Å, respectively] are similar to those in the complex $[Au(PPh_3)(qncd)]BF_4^{3d}$ [2.11(1) and 2.240(4) Å, respectively]. The cationic nature of 1 and the large PPh₃ groups are probably responsible for the absence of Au ••• Au contacts.

Experimental

The IR, C, H and N analyses, conductance measurements and melting point determinations were carried out as described elsewhere.⁹ The NMR spectra were recorded in CDCl₃ on a Varian Unity 300 spectrometer and conductivity measurements were carried out in acetone. Chemical shifts are referred to SiMe₄ (¹H and ¹³C) or external H₃PO₄ (³¹P). The following reagents were commercially available: CF₃SO₃H, NH₂(C₆H₄OMe-4) (Merck), [NHMe₃]Cl (Fluka), NHEt₂, NH₂(C₆H₄NO₂-2) (Aldrich), NHPh₂ (Probus). The compound [Au(acac)(PPh₃)] was prepared following a literature method.¹²

Syntheses.—[NHMe₃][ClO₄]. To a solution of [NHMe₃]Cl (1 g, 10.46 mmol) in acetone (20 cm³) was added NaClO₄·H₂O (1.47 g, 10.46 mmol) and the suspension stirred for 30 min. It was then filtered through Celite, the resulting solution concentrated (2 cm³) and diethyl ether (20 cm³) added to precipitate [NHMe₃][ClO₄] (1.33 g, 92%) as a white solid which was washed with diethyl ether (2 × 5 cm³) and air dried. M.p. 234 °C (Found: C, 22.65; H, 6.50; N, 8.55. Calc. for C₃H₁₀ClNO₄: C, 22.60; H, 6.30; N, 8.80%). $\Lambda_{\rm M} = 146 \,\Omega^{-1} \,{\rm cm^2} \,{\rm mol^{-1}} \,(1.35 \times 10^{-3} \,{\rm mol} \,{\rm dm^{-3}}). \,{\rm NMR}: {}^{1}{\rm H}, \delta 3.12$ (s, 9 H, Me), 4.16 (br, 1 H, NH). IR: v(NH) 3128 cm⁻¹.

 $[NH_2Et_2][CF_3SO_3]$. To a solution of $NHEt_2$ (98%, 1 cm³, 9.47 mmol) in diethyl ether (20 cm³) HO₃SCF₃ (Merck, 0.83



Fig. 1 The structure of complex 1

Table 1 Selected bond lengths (Å) and angles (°) for compound 1

Au-N P-C(21) P-C(31) N-C(3)	2.108(7) 1.804(10) 1.807(9) 1.482(11)	Au-P P-C(11) N-C(2) N-C(1)	2.231(2) 1.804(9) 1.472(12) 1.487(10)
N-Au-P	179.3(2)	C(21)-P-C(11)	107.9(4)
C(21) - P - C(31)	104.5(4)	C(11)-P-C(31)	105.7(4)
C(21)-P-Au	113.0(3)	C(11)-P-Au	112.6(3)
C(31)-P-Au	112.5(3)	C(2)-N-C(3)	108.6(7)
C(2) - N - C(1)	109.1(8)	C(3) - N - C(1)	109.5(8)
C(2)–N–Au	109.3(6)	C(3)-N-Au	110.2(6)
C(1)-N-Au	110.1(5)		. ,

cm³, 9.47 mmol) was added dropwise. A white solid precipitated immediately which was washed with diethyl ether (2 × 5 cm³), filtered off and air dried (381 mg, 18%). M.p. 121 °C (Found: C, 27.35; H, 5.75; N, 6.45; S, 14.60. Calc. for $C_5H_{12}F_3NO_3S$: C, 26.90; H, 5.40; N, 6.25; S, 14.35%). $\Lambda_M = 85 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (7.2 × 10⁻⁴ mol dm⁻³). NMR: ¹H, δ 1.35 (t, 6 H, Me), 3.23 (m, 4 H, CH₂), 7.69 (m br, 2 H, NH). IR: v(NH) 3156, 3054 cm⁻¹.

[NH₂Ph₂][CF₃SO₃]. Similarly, [NH₂Ph₂][CF₃SO₃] (350 mg, 18%) was obtained from NHPh₂ (1 g, 5.91 mmol) in diethyl ether (10 cm³) and CF₃SO₃H (0.8 cm³, 9.1 mmol). M.p. 135 °C (Found: C, 49.50; H, 3.90; N, 4.55; S, 9.50. Calc. for C₁₃H₁₂F₃NO₃S: C, 48.90; H, 3.80; N, 4.40; S, 10.05%). $\Lambda_{\rm M} = 106 \,\Omega^{-1} \, {\rm cm}^2 \, {\rm mol}^{-1} (5.0 \times 10^{-4} \, {\rm mol} \, {\rm dm}^{-3})$. ¹H NMR: δ7.39–7.87 (m, Ph). IR: v(NH) 3184 cm⁻¹.

 $[NH_3(C_6H_4NO_2-2)][CF_3SO_3]. Similarly, [NH_3(C_6H_4-NO_2-2)][CF_3SO_3] (650 mg, 63\%) was obtained from a solution of NH_2(C_6H_4NO_2-2) (98\%, 500 mg, 3.55 mmol) in diethyl ether (20 cm³) and HO_3SCF_3 (0.5 cm³, 5.7 mmol). M.p. 148 °C (Found: C, 29.70; H, 2.50; N, 10.00; S, 10.75. Calc. for C_7H_7F_3N_2O_5S: C, 29.15; H, 2.45; N, 9.70; S, 11.10\%). A_M = 94 \Omega^{-1} cm^2 mol^{-1} (6.9 \times 10^{-4} mol dm^{-3}). NMR: ^1H, \delta 7.96 (m, 2 H), 8.06 (m, 1 H), 8.43 (m, 1 H). The ¹H NMR spectrum shows the presence of a small amount of 2-nitroaniline in equilibrium with the ammoniun salt. IR: v(NH) 3119 cm⁻¹.$

[NH₃(C₆H₄OMe-4)][CF₃SO₃]. Similarly, [NH₃(C₆H₄-OMe-4)][CF₃SO₃] (820 mg, 92%) was obtained from a solution of NH₂(C₆H₄OMe-4) (400 mg, 3.25 mmol) in diethyl ether (15 cm³) and CF₃SO₃H (0.3 cm³, 3.25 mmol). M.p. 232 °C (Found: C, 35.35; H, 3.80; N, 5.20; S, 11.65. Calc. for C₈H₁₀F₃NO₄S: C, 35.15; H, 3.70; N, 5.15; S, 11.75%). $\Lambda_{\rm M} =$ 115 Ω⁻¹ cm² mol⁻¹ (7.32 × 10⁻⁴ mol dm⁻³). ¹H NMR: δ 3.87 (s, 3 H, OMe), 7.11, 7.16, 7.47, 7.52 (AA'BB' system). IR: v(NH) 3073 cm⁻¹.

[Au(PPh₃)(NMe₃)][ClO₄] 1. To a suspension of [Au-

Table 2 Atomic coordinates ($\times 10^4$) for compound 1

Atom	x	У	Ζ
Au	3 598.1(4)	2 878.9(3)	4 273.69(12)
Р	3 367(2)	4 766(2)	3 866.7(8)
Ν	3 836(8)	1 089(7)	4 652(3)
C(1)	3 771(12)	8(7)	4 277(4)
C(2)	5 209(10)	1 060(10)	4 913(4)
C(3)	2 712(10)	923(10)	5 040(4)
C(11)	2 398(10)	4 619(9)	3 276(3)
C(12)	1 223(10)	3 836(9)	3 267(3)
C(13)	432(10)	3 718(11)	2 832(4)
C(14)	807(12)	4 364(12)	2 397(4)
C(15)	2 004(11)	5 147(11)	2 395(4)
C(16)	2 779(12)	5 285(10)	2 837(4)
C(21)	5 033(10)	5 526(10)	3 725(3)
C(22)	6 255(10)	4 772(10)	3 697(3)
C(23)	7 512(11)	5 382(11)	3 586(4)
C(24)	7 599(11)	6 686(10)	3 488(4)
C(25)	6 392(11)	7 409(10)	3 507(3)
C(26)	5 120(10)	6 856(10)	3 631(3)
C(31)	2 428(9)	5 956(8)	4 242(4)
C(32)	2 767(10)	6 051(10)	4 761(3)
C(33)	2 114(10)	6 959(10)	5 064(3)
C(34)	1 096(9)	7 758(10)	4 868(3)
C(35)	743(9)	7 660(8)	4 352(3)
C(36)	1 394(10)	6 766(8)	4 036(3)
Cl(1)	9 038(2)	1 041(2)	3 994.0(8)
O(1)	9 301(10)	1 170(8)	4 530(3)
O(2)	8 381(9)	2 179(8)	3 801(3)
O(3)	8 171(9)	-66(8)	3 917(3)
O(4)	10 339(9)	854(9)	3 735(3)
C(4)	2 971(15)	908(14)	2 885(5)
Cl(2)	3 249(4)	-755(4)	2 826(2)
Cl(3)	4 535(5)	1 742(4)	2 994(2)

(acac)(PPh₃)] (500 mg, 0.89 mmol) in degassed acetone (10 cm³), [NHMe₃][ClO₄] (143 mg, 0.89 mmol) was added and the reaction mixture stirred under a nitrogen atmosphere in an icewater bath for 1.5 h. The resulting solution was concentrated (2 cm³) and diethyl ether (20 cm³) added to precipitate 1 (523 mg, 95%) as a white solid which was recrystallized twice from dichloromethane-diethyl ether. M.p. 178 °C (decomp.) (Found: C, 40.70; H, 4.20; Au, 31.55; N, 2.20. Calc. for $C_{21}H_{24}Au$ -CINO₄P: C, 40.80; H, 4.00; Au, 31.90; N, 2.25%). $\Lambda_{\rm M} = 90 \ \Omega^{-1}$ cm² mol⁻¹ (3.24 × 10⁻⁴ mol dm⁻³). NMR: ¹H, δ 2.97 (s, 9 H, Me), 7.4–6.1 (m, 15 H, Ph); 31 P, δ 30.42 (s); 13 C, δ 134.5 (d, ${}^{3}J_{PC}$ 13), 133.1 (s), 130.0 (d, ${}^{2}J_{PC}$ 12), 127.1 (d, ${}^{1}J_{PC}$ 64 Hz), 52.7 (s, Me).

 $[Au(PPh_3)(NHEt_2)][CF_3SO_3]$ 2. To a suspension of $[Au(acac)(PPh_3)]$ (179.5 mg, 0.32 mmol) in diethyl ether (15 cm³) was added [NH₂Et₂][CF₃SO₃] (71.7 mg, 0.32 mmol). Immediate reaction was observed with formation of an oil which converted into a powder upon stirring in diethyl ether for 1 h. It was filtered off, washed with diethyl ether (10 cm³) and recrystallized from acetone-diethyl ether to give 2 (191 mg, 87%). M.p. 124 °C (Found: C, 40.00; H, 3.70; Au, 29.00; N, 1.95; S, 4.60. Calc. for $C_{23}H_{26}AuF_3NO_3PS$: C, 40.55; H, 3.85; Au, 29.0; N, 2.05; S, 4.70%). $\Lambda_M = 101 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ $(2.96 \times 10^{-4} \text{ mol dm}^{-3})$. NMR: ¹H, δ 1.48 (t, 6 H, Me, ³J_{HH} = 7 Hz), 3.2 (m, 4 H, CH₂), 7.4–7.6 (m, 15 H, Ph); ³¹P, δ 30.89 (s). IR: v(NH) 3149 cm⁻¹

[Au(PPh₃)(NHPh₂)][CF₃SO₃] 3. To a suspension of $[Au(acac)(PPh_3)]$ (60 mg, 0.11 mmol) in diethyl ether (10 cm³), [NH₂Ph₂][CF₃SO₃] (40 mg, 0.11 mmol) was added. The resulting solution gave, on stirring, a suspension which was filtered after 1 h. The cream solid was washed with diethyl ether (5 cm³) and recrystallized from dichloromethane-diethyl ether to give 3 (67 mg, 78%) as a white solid. M.p. 137 °C (decomp.) (Found: C, 47.60; H, 3.35; Au, 26.10; N, 1.80; S, 4.45. Calc. for C₃₁H₂₆AuF₃NO₃PS: C, 47.90; H, 3.35; Au, 25.35; N, 1.80; S, 4.10%). $\Lambda_{\rm M} = 110 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1} \ (9.25 \times 10^{-5} \ {\rm mol} \ {\rm dm}^{-3}).$

NMR: ¹H, δ 7.0-7.8 (m, 25 H, Ph), 8.84 (s br, 1 H, NH); ³¹P, δ 28.89 (s).

 $[Au(PPh_3){NH_2(C_6H_4NO_2-2)}][CF_3SO_3]$ 4. To a solution of $[NH_3(C_6H_4NO_2-2)][CF_3SO_3]$ (81.6 mg, 0.28 mmol) in diethyl ether (15 cm³) was added [Au(acac)(PPh₃)] (158 mg, 0.28 mmol). The resulting suspension was stirred for 3 h and filtered to give 4 (68 mg, 32%) which was washed with diethyl ether (10 cm³) and air dried. M.p. 150 °C (decomp.) (Found: C, 40.45; H, 2.60; Au, 25.70; N, 3.35; S, 4.35. Calc. for $C_{25}H_{21}AuF_3N_2O_5PS: C, 40.25; H, 2.85; Au, 26.40; N, 3.75; S, 4.30%). A_M = 99 \Omega^{-1} cm^2 mol^{-1} (2.84 \times 10^{-4} mol dm^{-3}).$ NMR: ¹H, δ 7.02 ('t', 1 H, NH₂C₆H₄NO₂-2), 7.4–7.7 (m, 15 H, DPL - 2 H) NH C (H $PPh_3 + 2$ H, $NH_2C_6H_4NO_2-2$), 8.17 ('d', 1 H, $NH_2C_6H_4-$ NO₂-2); ³¹P, δ 28.99 (s). IR: v(NH) 3214 cm⁻¹

 $[Au(PPh_3){NH_2(C_6H_4OMe-4)}][CF_3SO_3]$ 5. To a suspension of [Au(acac)(PPh₃)] (174 mg, 0.31 mmol) in diethyl ether (20 cm³) was added [NH₃(C₆H₄OMe-4)][CF₃SO₃] (105 mg, 0.31 mmol). Immediate reaction was observed with formation of an oily solid which converted into a powder upon stirring in diethyl ether for 1 h. It was filtered off, washed with diethyl ether (5 cm³) and air dried to give 5 (189 mg, 83%). M.p. 131 °C (decomp.) (Found: C, 42.25; H, 3.05; Au, 27.50; N, 1.85; S, 4.40. Calc. for C₂₆H₂₄AuF₃NO₄PS: C, 42.70; H, 3.30; Au, 26.95; N, 1.85; S, 4.40%). $\Lambda_{\rm M} = 52 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1} \ (4.65 \times 10^{-4})^{-4}$ mol dm⁻³). NMR: ¹H, δ 3.71 (s, 3 H, Me), 6.73, 6.76, 7.24, 7.27 (AA'BB', 4 H), 7.4–7.6 (m, 15 H, PPh₃); ³¹P, δ 31.07 (s). IR: v(NH) 3173, 3092 cm⁻¹.

Crystal Structure Determination of Compound 1.-Crystal data. C₂₂H₂₆AuCl₃NO₄P, orthorhombic, space group P2₁2₁2₁, $a = 9.498(2), b = 10.322(2), c = 26.154(4) \text{ Å}, U = 2564.1 \text{ Å}, Z = 4, D_c = 1.820 \text{ Mg m}^{-3}, F(000) = 1368, \lambda(Mo-K\alpha) = 0.710 73 \text{ Å}, \mu = 6.1 \text{ mm}^{-1}, T = -130 \text{ °C}. A colourless prism ca. 0.5 × 0.2 × 0.15 mm was mounted on a glass fibre in$ inert oil and transferred to the cold-gas stream of the diffractometer (Stoe STADI-4 with Siemens LT-2 low temperature attachment). A total of 6114 reflections were collected to 20 55°, of which 5288 were independent (R_{int} 0.0359) after an absorption correction based on ψ scans (transmissions of 0.56–0.99). Cell constants were refined from $\pm \omega$ values of 74 reflections in the range 20-23°

Structure solution and refinement. The structure was solved by the heavy-atom method and refined on F^2 (ref. 13). Hydrogen atoms were included using a riding model or as rigid methyl groups. The absolute structure was determined by the xparameter -0.022(11).¹⁴ The final $wR(F^2)$ was 0.091 for all reflections, with a conventional R(F) of 0.043, for 292 parameters and 192 restraints; S = 1.05, max. $\Delta/\sigma 0.002$, max. $\Delta \rho$ 0.75 e Å⁻³. Selected bond lengths and angles are given in Table 1 and final atomic coordinates in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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