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Synthesis, Structures, and Reactivity of Four-Electron-Donor η^2-Organonitrile, Carbonyl Oxo, and Carbonyl Thio Complexes of Tungsten

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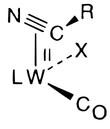
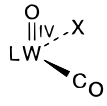
Summary: Reactions of $LW(S_2PR_2)(CO)_2$ *(L = hydrotris(3,5-dimethylpyrazol-1-yl)borate) with pyridine N-oxide produce carbonyl oxo complexes,* $LW^{IV}O(S_2PR_2)(CO)$*. Thermal decarbonylation of* $LWX(CO)_2$ *(X = halide) complexes in organonitrile solvents produces 4-electron-donor nitrile complexes,* $LW^{II}X(\eta^2\text{-}RCN)(CO)$*, which react with* $NH_4[S_2PR_2]$ *to form* $LW^{II}(S_2PR_2)(\eta^2\text{-}RCN)(CO)$*. Reactions of the nitrile complexes with propylene sulfide result in high yields of the carbonyl thio complexes* $LW^{IV}SX(CO)$ *or* $LW^{IV}S(S_2PR_2)(CO)$*. The structures of* $LW^{IV}O(S_2PPh_2)(CO)$*, (R)-*$LW^{II}(S_2PR^*_2)(\eta^2\text{-}MeCN)(CO)$ *(R* = (−)-mentholate), and* $LW^{IV}S(S_2PPh_2)(CO)$ *can be rationalized in terms of the π-bonding requirements of the electronically disparate π-acid and π-base ligands.*

The synthesis and reactivity of complexes containing electronically disparate ligands, e.g. strong π-acids and π-bases, have attracted growing attention.[1−7] This communication describes the synthesis, characterization, and reactivity of carbonyl(η^2-nitrile)tungsten(II), carbonyloxotungsten(IV), and carbonylthiotungsten(IV) complexes (**A**−**C**; L = hydrotris(3,5-dimethylpyrazol-1-yl)borate, X = monoanion) which combine π-acid carbonyl and π-base nitrile or chalcogenido ligands at a common metal center. These novel complexes have emerged from the development of a low-valent synthetic approach to bis(chalcogenido)tungsten(VI) complexes which involves successive two-electron-oxidation/atom-transfer reactions, beginning with $[LW^0(CO)_3]^-$,[8] and progressing through $LW^{II}X(CO)_x$ (x = 2, 3),[5,9−12] $LW^{II}X(\eta^2\text{-}RCN)(CO)$ (R = Me, Et, Ph), and $LW^{IV}EX(CO)$ (E = O, S) to $LW^{VI}E_2X$.[13,14] Quality (non-disordered) crystal structures of $LW^{II}(S_2PR^*_2\text{-}S)(\eta^2\text{-}MeCN)(CO)$ (R* = (−)-mentholate), $LW^{IV}O(S_2PPh_2\text{-}S)(CO)$, and $LW^{IV}S(S_2PPh_2\text{-}S)(CO)$ confirm the formulations and provide the first definitive metrical data for the metal cores in **A**−**C**, the structure of $LW^{IV}S(S_2PPh_2)(CO)$ being the first reported for any carbonylthiometal complex.



A



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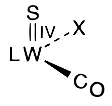

C

We have described the synthesis of the carbonyloxotungsten(IV) complexes $LW^{IV}OX(CO)$ (X = I, Br)[5] and $LW^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)L$[6] but due to crystal disorder were unable to precisely define their structures. Metathesis of $LWX(CO)_2$ with $NH_4[S_2PPh_2]$ resulted in the formation of $LW(S_2PPh_2)(CO)_2$, which was oxidized to air-stable, pink $LW^{IV}O(S_2PPh_2\text{-}S)(CO)$ by pyridine *N*-oxide.[15] This complex exhibited a strong ν(CO) band at 1985 cm^{-1}, a strong ν(W═O) band at 952 cm^{-1}, and ^{1}H and ^{13}C NMR spectra consistent with C_1 symmetry. A ^{13}C resonance at δ 274 ($^1J_{WC}$ = 190 Hz) was assigned to the carbonyl carbon atom. The crystal structure of the complex confirmed the presence of the carbonyloxotungsten moiety (Figure 1).[16] The mononuclear, distorted-octahedral complex contains a facially tridentate L ligand and mutually *cis* oxo, carbonyl, and monodentate dithiophosphinate ligands. The W−O(2) distance of 1.702(4) Å is comparable to that found in $WOCl_2(CO)(PMePh_2)_2$[2−4] and is typical of oxotungsten(IV) complexes.[17] The carbonyl ligand is perpendicular to the W═O axis, with an O(2)−W−C(1) angle of 91.2(2)°. The W−C(1)−O(1) angle of 171.5(5)° reflects a steric interaction between the carbonyl ligand and the uncoordinated sulfur atom S(2). The carbonyl stretching

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(15) A suspension of $LW(S_2PPh_2)(CO)_2$ (1.23 g, 1.56 mmol) in tetrahydrofuran (30 mL) was cooled to 0 °C, and pyridine *N*-oxide (0.30 g, 3.15 mmol) was added. The reaction mixture was stirred for 1 h and the solvent evaporated. The residue was chromatographed on silica using dichloromethane/hexane (3/1) to yield a pink-brown fraction. The product was recrystallized from dichloromethane/methanol as pink crystals, which were filtered, washed with methanol, and dried *in vacuo*. Yield: 0.76 g, 63%.

(16) Crystallographic data for $LWO(S_2PPh_2)(CO)$: $C_{28}H_{32}BN_6O_2PS_2W$, fw 774.4, triclinic space group $P1$, with a = 11.281(2) Å, b = 16.228(6) Å, c = 9.338(2) Å, α = 96.33(2)°, β = 107.34(2)°, γ = 73.03(2)°, V = 1560.3(8) Å^3, and D_c = 1.648 g cm^{-3} for Z = 2. The structure was solved by direct methods and refined by a full-matrix least-squares procedure using 5198 data to a conventional R value of 0.033 (R_w = 0.035). In all structural figures, the numbering of the pyrazole rings parallels that shown for the ring containing N(11).

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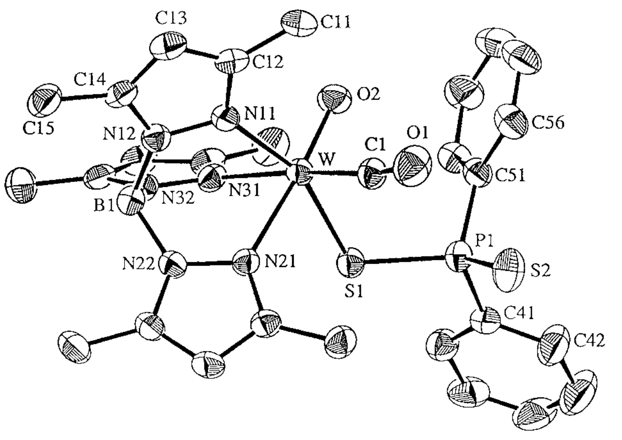

Figure 1. Molecular structure of LW^{IV}O(S$_2$PPh$_2$-*S*)(CO). Selected bond lengths (Å) and angles (deg) are as follows: W−O(2) = 1.702(4), W−C(1) = 1.996(5), W−S(1) = 2.454(1), W−N(11) = 2.172(4), W−N(21) = 2.287(4), W−N(31) = 2.198(4), C(1)−O(1) = 1.151(6); O(2)−W−S(1) = 102.4(1), O(2)−W−C(1) = 91.2(2), O(2)−W−N(11) = 94.9(2), O(2)−W−N(21) = 173.7(2), O(2)−W−N(31) = 95.7(2), S(1)−W−C(1) = 96.7(2), S(1)−W−N(11) = 159.8(1), S(1)−W−N(21) = 83.8(1), S(1)−W−N(31) = 84.7(1), C(1)−W−N(11) = 93.2(2), C(1)−W−N(21) = 88.6(2), C(1)−W−N(31) = 172.5(2), N(11)−W−N(21) = 78.9(1), N(11)−W−N(31) = 83.3(1), N(21)−W−N(31) = 84.2(1), W−S(1)−P(1) = 110.45(7).

frequencies of LWO(S$_2$PPh$_2$)(CO) (1985 cm^{-1}) and WOCl$_2$(CO)(PMePh$_2$)$_2$ (2006 cm^{-1}) are consistent with greater π-back-bonding to the carbonyl ligand in the former. As previously expounded,[4] the disposition of the π-acid carbonyl and π-base oxo ligands is consistent with optimal ligand−metal π-orbital overlap.

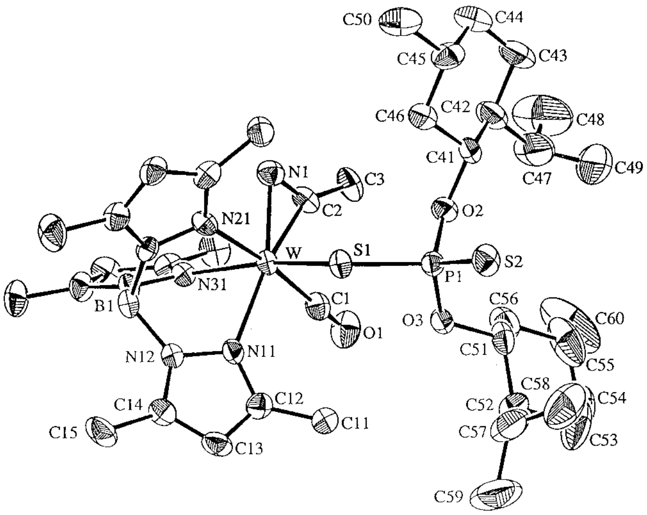

Figure 2. Molecular structure of (*R*)-LW^{II}(S$_2$PR*$_2$-*S*)(η^2-MeCN)(CO). Selected bond lengths (Å) and angles (deg) are as follows: W−C(1) = 1.940(8), W−N(1) = 2.033(6), W−C(2) = 2.051(7), W−S(1) = 2.435(2), W−N(11) = 2.241(6), W−N(21) = 2.262(6), W−N(31) = 2.183(6); C(1)−W−S(1) = 95.9(3), C(1)−W−C(2) = 72.5(3), C(1)−W−N(1) = 107.3(3), C(1)−W−N(11) = 88.9(3), C(1)−W−N(21) = 172.4(3), C(1)−W−N(31) = 93.8(4), S(1)−W−C(2) = 101.2(3), S(1)−W−N(1) = 100.2(2), S(1)−W−N(11) = 87.0(2), S(1)−W−N(21) = 82.9(2), S(1)−W−N(31) = 162.6(1), C(2)−W−N(1) = 34.9(3), C(2)−W−N(11) = 160.3(3), C(2)−W−N(21) = 115.0(3), C(2)−W−N(31) = 95.5(3), N(1)−W−N(11) = 161.2(3), N(1)−W−N(21) = 80.2(2), N(1)−W−N(31) = 90.8(3), N(11)−W−N(21) = 83.6(2), N(11)−W−N(31) = 78.7(3), N(21)−W−N(31) = 85.6(3), W−S(1)−P(1) = 116.5(1).

Thermal decarbonylation of LWX(CO)$_3$ (X = Cl, Br, I) is known to form paramagnetic LWX(CO)$_2$ complexes.[10−12] However, prolonged thermal decarbonylation of LWX(CO)$_2$ in acetonitrile resulted in the formation of the novel four-electron-donor η^2-acetonitrile complexes LW^{II}X(η^2-MeCN)(CO).[18] Spectroscopic and structural data were consistent with the formation of a single isomer in each case. These complexes exhibited a strong ν(CO) band at ca. 1910 cm^{-1}, a weak ν(C≡N) band at ca. 1695 cm^{-1}, and ^{1}H and ^{13}C NMR spectra consistent with C_1 symmetry. The η^2-acetonitrile methyl group resonated around δ 3.92 in ^{1}H NMR spectra (established by the disappearance of the resonance upon selective deuteration). Carbon-13 resonances at ca. δ 202 ($^1J_{WC} \approx 26$ Hz) and δ 226 ($^1J_{WC} \approx 155$ Hz) were assigned to the nitrile and carbonyl carbon atoms, respectively. To circumvent disorder (present in samples initially examined) and permit a definitive structural characterization of the η^2-acetonitrile ligand, a new chiral dialkyldithiophosphate ligand was introduced at the tungsten center by methathesis of LWI(η^2-MeCN)(CO) with NH$_4$[S$_2$PR*$_2$];[19,20] air-stable, emerald green LW(S$_2$PR*$_2$-*S*)(η^2-MeCN)(CO) was isolated as an 8:1 diastereomeric mixture (established by ^{1}H and ^{13}C NMR). The structure of (*R*)-LW(S$_2$PR*$_2$)(MeCN)(CO) (Figure 2) was determined by X-ray crystallography.[21] The seven-coordinate complex contains a facially tridentate L ligand, carbonyl and monodentate dithiophosphate ligands, and a side-on *C*,*N*-bound acetonitrile ligand. The W(η^2-MeCN) fragment is characterized by the following structural parameters: W−N(1) = 2.033(6) Å, W−C(2) = 2.051(7) Å, C(2)−N(1) = 1.225(9) Å, C(2)−W−N(1) = 34.9(3)°, W−C(2)−C(3) = 150.0(7)°, and N(1)−C(2)−C(3) = 138.1(8)°. The C(2)−N(1) bond in the complex is lengthened by 0.066 Å compared to that of the free ligand,[22] consistent with a reduction in C−N bond order as a result of π-interactions with the tungsten. The non-hydrogen atoms of the W(η^2-MeCN)(CO) framework are very nearly planar, with a *syn* relationship for the methyl and carbonyl groups. The *syn* orientation is sterically preferred, but an electronic

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[18] Synthesis of LW^{II}I(MeCN)(CO): A solution of LWI(CO)$_3$ (2.24 g, 3.24 mmol) in dry acetonitrile (30 mL) was refluxed under nitrogen for 4 h and then cooled to −4 °C overnight. The gold-colored crystalline solid was filtered off, washed with cold acetonitrile (5 mL) and dried *in vacuo*. Yield: 1.36 g, 62%. This product was suitable for synthetic work, but analytical samples required purification by column chromatography on silica using dichloromethane/hexane (2/1). Related LWX(η^2-RCN)(CO) (R = Et, Ph) complexes can be prepared but are relatively unstable in solution.

[19] Reaction of P$_4$S$_{10}$ with (1*R*,2*S*,5*R*)-(−)-menthol in refluxing toluene, followed by filtration, treatment of the filtrate with ammonia, and addition of hexane yielded NH$_4$[S$_2$PR*$_2$] as white crystals.

[20] A suspension of LWI(MeCN)(CO) (1.17 g, 1.73 mmol) and NH$_4$[S$_2$PR*$_2$] (0.75 g, 1.77 mmol) in acetonitrile (25 mL) was heated to 80 °C for 30 min and then cooled to room temperature. The solvent was evaporated and the residue chromatographed on silica−dichloromethane to yield a green fraction. The product was recrystallized from dichloromethane/hexane as green crystals, which were filtered, washed with hexane and dried *in vacuo*. Yield: 0.82 g, 50%.

[21] Crystallographic data for (*R*)-LW(S$_2$PR*$_2$)(MeCN)(CO): C$_{38}$H$_{63}$BN$_7$O$_3$PS$_2$W, fw 955.7, orthorhombic space group $P2_12_12_1$, with a = 17.753(7) Å, b = 18.867(5) Å, c = 13.394(4) Å, V = 4486(2) Å^3, and D_c = 1.415 g cm^{-3} for Z = 4. Analysis as in ref 16 for 4040 data gave R = 0.033 (R_w = 0.031); the absolute structure is based on the conformation of (−)-mentholate. The W···B vector is taken as the imaginary, single binding point of the L ligand, which is assigned lowest priority. The priority assignments of the other ligands are as follows: S$_2$PR*$_2^-$ > η^2-MeCN (one site) > CO.

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structure akin to that of four-electron-donor alkyne complexes such as LWI(RC≡CR)(CO)[9,23] dictates the observed orientation of the carbonyl and acetonitrile ligands. Structurally and spectroscopically, the W(η^2-MeCN) moieties of LWX(η^2-MeCN)(CO) are closely related to those of [WCl(η^2-MeCN)(bpy)(PMe$_3$)$_2$]PF$_6$[24a] (bpy = 2,2′-bipyridine) and WCl$_2$(η^2-MeCN)(PMe$_3$)$_3$,[24b] the only other known four-electron-donor η^2-acetonitrile complexes. All other η^2-acetonitrile complexes exhibit structures and spectroscopic properties consistent with a two-electron-donor description.[25] The activation of nitriles by metal centers has many potential synthetic applications and has attracted considerable attention.[26,27]

Attempts to prepare LW^{IV}SX(CO) by reaction of LWX(CO)$_x$ (x = 2, 3) with the sulfur atom donor propylene sulfide produced the (μ-thio)ditungsten(II) complexes [LW^{II}(CO)$_2$]$_2$(μ-S).[11] We concluded that the use of monocarbonyltungsten(II) starting materials would favor the formation of the desired LWSX(CO) complexes, and indeed, reaction of LWX(η^2-MeCN)(CO) with propylene sulfide produced high yields of LWSX(CO).[28] The dithio acid derivatives (X = S$_2$PR$_2^-$; R = OEt, OPr^i, R*, Ph) were readily accessible by a similar pathway. The carbonyl thio complexes exhibited a strong ν(CO) band at ca. 1960 cm^{-1}, a weak ν(W=S) band at ca. 511 cm^{-1}, and ^{1}H and ^{13}C NMR spectra consistent with C_1 symmetry. A ^{13}C resonance at ca. δ 273 ($^1J_{WC} \approx$ 164 Hz) was assigned to the carbonyl carbon atom. The crystal structure of LWS(S$_2$PPh$_2$-*S*)(CO) confirmed the presence of the carbonylthiotungsten moiety (Figure 3);[29] it constitutes the first structural characterization of any monomeric carbonylthiometal complex.

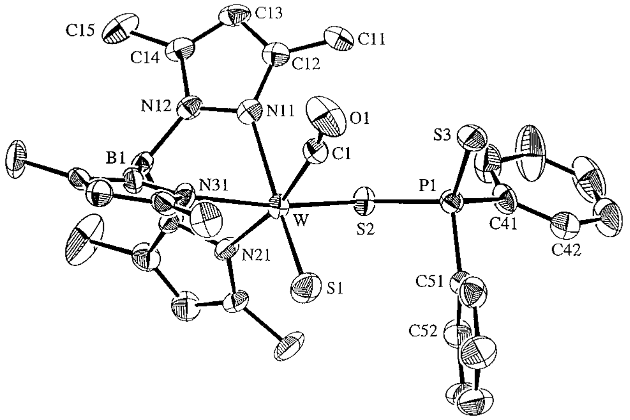

Figure 3. Molecular structure of LW^{IV}S(S$_2$PPh$_2$-*S*)(CO). Selected bond lengths (Å) and angles (deg) are as follows: W−S(1) = 2.132(4), W−S(2) = 2.446(3), W−C(1) = 2.01(1), W−N(11) = 2.29(1), W−N(21) = 2.18(1), W−N(31) = 2.19(1), C(1)−O(1) = 1.11(2); S(1)−W−S(2) = 99.9(2), S(1)−W−C(1) = 89.5(4), S(1)−W−N(11) = 171.5(3), S(1)−W−N(21) = 102.1(3), S(1)−W−N(31) = 96.7(3), S(2)−W−C(1) = 97.5(4), S(2)−W−N(11) = 84.5(3), S(2)−W−N(21) = 84.5(3), S(2)−W−N(31) = 161.2(3), C(1)−W−N(11) = 82.7(5), C(1)−W−N(21) = 167.7(4), C(1)−W−N(31) = 91.5(5), N(11)−W−N(21) = 85.4(4), N(11)−W−N(31) = 80.2(4), N(21)−W−N(31) = 83.3(4), W−S(2)−P(1) = 112.9(2).

The molecule exhibits a distorted-octahedral geometry comprised of a facially tridentate L ligand and mutually *cis* thio, carbonyl, and monodentate dithiophosphinate ligands. The W−S(1) distance of 2.132(4) Å is typical of thiotungsten complexes.[17] The W−C(1)−O(1) angle of 168(1)° again reflects a steric interaction between the carbonyl ligand and uncoordinated sulfur S(3). The enhancement of this interaction relative to that in the carbonyl oxo complexes is reflected in the lower energy of the ν(CO) band of the carbonyl thio complexes. The disposition of the carbonyl and thio ligands is nicely rationalized in terms of orbital overlap.[4]

In conclusion, novel tungsten complexes combining electronically disparate π-acid carbonyl and π-base four-electron-donor nitrile or chalcogenido ligands have been prepared and characterized. The structures of the complexes are consistent with the mutual electronic requirements of the π-acid and π-base ligands involved in each case. Finally, the carbonyl chalcogenido complexes undergo further two-electron atom-transfer reactions,[30] permitting the synthesis of dioxo-, oxothio-, and dithiotungsten(VI) species.[13,14] The generation of a complete series of W(0), W(II), W(IV), and W(VI) complexes via oxidation/atom-transfer reactions demonstrates the viability of the selective synthesis of high-valent chalcogenido complexes via low-valent routes.

Acknowledgment. We gratefully acknowledge the financial support of the Australian Research Council.

Supporting Information Available: Listings of fractional atomic coordinates, thermal parameters, hydrogen atom parameters, and all bond distances and angles, for the three crystal structures in this paper and a table of elemental analyses for all of the compounds synthesized in this paper (26 pages). Ordering information is given on any current masthead page.

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(26) The elaboration of bound nitriles has been highlighted in the recent work of Templeton et al.: (a) Feng, S. G.; Templeton, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6477. (b) Feng, S. G.; Templeton, J. L. *Organometallics* **1992**, *11*, 1295. (c) Feng, S. G.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 1765. (d) Young, C. G.; Philipp, C. C.; White. P. S.; Templeton, J. L. *Inorg. Chem.* **1995**, *34*, 6412.

(27) In an attempt to prepare LWOI(CO), LWI(MeCN)(CO) was reacted with pyridine *N*-oxide. The product is tentatively characterized as the η^2-acetonitrile *N*-oxide complex LWI(MeCN→O)(CO), by virtue of very strong ν(CO) and ν(N→O) bands at 1956 and 1260 cm^{-1}, respectively, and ^{13}C NMR resonances at δ 182 ($^1J_{WC}$ = 35 Hz, CN) and δ 270 ($^1J_{WC}$ = 171 Hz, CO). Further characterization of this material is underway.

(28) A suspension of LW(S$_2$PPh$_2$)(η^2-MeCN)(CO) (0.80 g, 1.00 mmol) in 1:1 acetonitrile/THF (30 mL) was heated to 75 °C, and propylene sulfide (0.20 mL, 2.55 mmol) was added. The reaction mixture was heated for 30 min and then cooled to room temperature. The solvent was evaporated and the residue chromatographed on silica−dichloromethane/hexane (2/1) to yield a green fraction. The product was recrystallized from dichloromethane/methanol as green crystals, which were filtered, washed with methanol, and dried *in vacuo*. Yield: 0.45 g, 57%.

(29) Crystallographic data for LWS(S$_2$PPh$_2$)(CO)·0.5CHCl$_3$: C$_{28.5}$H$_{32.5}$BCl$_{1.5}$N$_6$OPS$_3$W, fw 850.1, orthorhombic space group *Fdd*2, with a = 32.242(6) Å, b = 41.145(6) Å, c = 10.352(4) Å, V = 13733(5) Å^3, and D_c = 1.644 g cm^{-3} for Z = 16. Analysis as in ref 16 for 2683 data gave R = 0.037 (R_w = 0.042). The chloroform molecule of solvation is disordered about a crystallographic 2-fold axis, and the absolute structure was determined on the basis of differences in Friedel pairs included in the data set.

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