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Insight into the structures of [$M(C_5H_4I)(CO)_3$] and [$M_2(C_{12}H_8)(CO)_6$] (M = Mn and Re) containing strong I···O and π(CO)–π(CO) interactions

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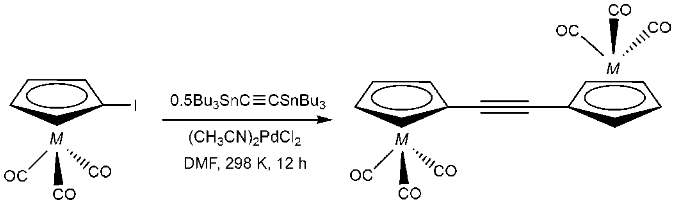
The compounds tricarbonyl(η^5-1-iodocyclopentadienyl)manganese(I), [$Mn(C_5H_4I)(CO)_3$], (I), and tricarbonyl(η^5-1-iodocyclopentadienyl)rhenium(I), [$Re(C_5H_4I)(CO)_3$], (III), are isostructural and isomorphous. The compounds [μ-1,2(η^5)-acetylenedicyclopentadienyl]bis[tricarbonylmanganese(I)] or bis(cymantrenyl)acetylene, [$Mn_2(C_{12}H_8)(CO)_6$], (II), and [μ-1,2(η^5)-acetylenedicyclopentadienyl]bis[tricarbonylrhenium(I)], [$Re_2(C_{12}H_8)(CO)_6$], (IV), are isostructural and isomorphous, and their molecules display inversion symmetry about the mid-point of the ligand C$\equiv$C bond, with the $(CO)_3M(C_5H_4)$ (M = Mn and Re) moieties adopting a *transoid* conformation. The molecules in all four compounds form zigzag chains due to the formation of strong attractive I···O [in (I) and (III)] or π(CO)–π(CO) [in (I) and (IV)] interactions along the crystallographic b axis. The zigzag chains are bound to each other by weak intermolecular C—H···O hydrogen bonds for (I) and (III), while for (II) and (IV) the chains are bound to each other by a combination of weak C—H···O hydrogen bonds and $\pi(Csp^2)$–$\pi(Csp^2)$ stacking interactions between pairs of molecules. The π(CO)–π(CO) contacts in (II) and (IV) between carbonyl groups of neighboring molecules, forming pairwise interactions in a sheared antiparallel dimer motif, are encountered in only 35% of all carbonyl interactions for transition metal–carbonyl compounds.

Comment

One of the rapidly growing fields in metalloorganic chemistry is the synthesis of new materials. Examples include dendrimers (Tomalia *et al.*, 1990; Stulgies *et al.*, 2005; Astruc *et al.*, 2008), staffanes (Kaszynski *et al.*, 1992), Diederich's carbon nets (Diederich & Rubin, 1992), and various novel electronic, photonic and magnetic materials (Barlow & O'Hare, 1997; Elschenbroich *et al.*, 2005; Kinnibrugh *et al.*, 2009). Because of the increasing interest in this area, we have focused our studies on structural investigations of the title compounds, (I)–(IV) (Figs. 1 and 2), which can be used as starting compounds for the construction of new materials (Sterzo *et al.*, 1989). This work reports the first structural studies of the monohalogenated derivatives (η^5-C_5H_4X)M(CO)$_3$ [for (I): M = Mn and X = I; for (III): M = Re and X = I] and the dinuclear [$(CO)_3MC_5H_4$]C$\equiv$C[$C_5H_4M(CO)_3$] compounds [for (II): M = Mn; for (IV): M = Re].



(I) M = Mn
(III) M = Re

(II) M = Mn
(IV) M = Re

The mean values of the geometric parameters for compounds (I)–(IV) are in accordance with those previously reported (Table 1) for 89 monosubstituted cymantrenes and 27 (η^5-C_5H_4X)Re(CO)$_3$ compounds, which were retrieved from the 2009 version of the Cambridge Structural Database (CSD; Allen, 2002) using *ConQuest* (Version 1.11; Macrae *et al.*, 2006), as well as with the unsubstituted compounds $C_5H_5M(CO)_3$ (M = Mn and Re) (Fitzpatrick, Le Page *et al.*, 1981; Cowie *et al.*, 1990). The monosubstituted (η^5-C_5H_4X)M(CO)$_3$ complexes (X = any atom; M = Mn and Re) were considered with the following search criteria: (*a*) three-dimensional coordinates and R < 0.10; (*b*) no errors; (*c*) no crystallographic disorder; (*d*) no polymer structures. The (O)C—Mn—C(O) angle is in accord with a tendency for decreasing the pyramidality of the M(CO)$_3$ fragment with increasing π-donor capacity of the cyclic polyene (Fitzpatrick, Le Page *et al.*, 1981): 88.22 (8)° for $(C_6H_6)Cr(CO)_3$ (Rees & Coppens, 1973), 90.0 (2)° for CpRe(CO)$_3$ (Fitzpatrick, Le Page & Butler, 1981), 92.02 (5)° for CpMn(CO)$_3$ (Cowie *et al.*, 1990), 95.6° for $(C_4H_4)Fe(CO)_3$ (Hall *et al.*, 1975) and 97.03 (3)° for $(C_4Ph_4)Fe(CO)_3$ (Dodge & Schomaker, 1965). The M—C—O bond angles do not differ significantly from 180°.

The M(CO)$_3$ (M = Mn and Re) fragment possess approximate C_{3v} symmetry, while coordination to the η^5-C_5H_4X ring lowers the molecular symmetry to C_1 (Fig. 3). Compounds (I)–(IV) possess different mutual dispositions of the carbonyl groups and η^5-C_5H_4X rings: the C6$\equiv$O1 carbonyl group for each of (I) and (III) is in an eclipsed position relative to the substituted C atom of the η^5-C_5H_4I ring, while the C7$\equiv$O1 carbonyl group of each of (II) and (IV) is in the *transoid* position with respect to the substitutent-bearing C atom (Figs. 3 and 4).

Compounds (II) and (IV) crystallize with the molecules lying across crystallographic inversion centers. Each molecule consists of two identical [$(CO)_3M(C_5H_4)$C$\equiv$] (M = Mn and

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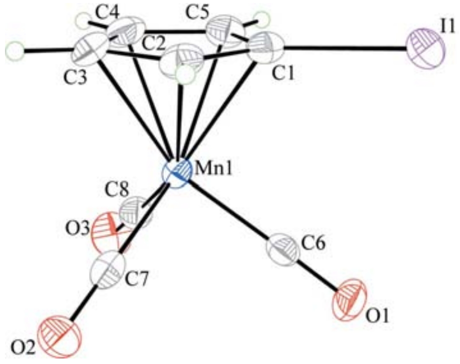

Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. The Re analog, (III), is isostructural. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

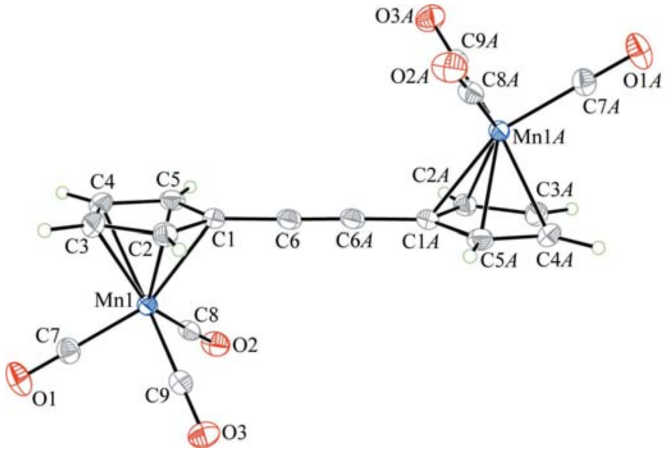

Figure 2
A view of the molecule of (II), showing the atom-numbering scheme. The Re analog, (IV), is isostructural. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Atoms labelled with the suffix *A* are at the symmetry position $(-x + 2, -y + 1, -z)$.

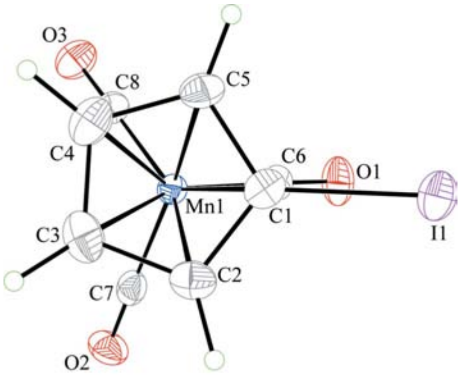

Figure 3
The conformation of (I), showing one CO group eclipsed by the halogen substituent on the C_5 ring.

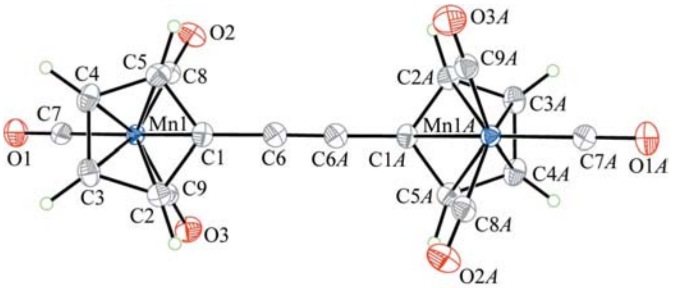

Figure 4
The conformation of (II), showing the CO group in a *transoid* position relative to the substituent on the C_5 ring.

Re) parts with the $M(CO)_3$ moieties in *transoid* positions. We suggest that (II) and (IV) adopt the *transoid* structure due to the presence of strong attractive intermolecular π(CO)–π(CO) interactions in the sheared parallel packing motif (see below). In contrast, the only analogous compound found in the literature, *viz.* $[(CO)_3Mn(C_5H_4)C{\equiv}C(C_7H_5)Cr(CO)_3]$-$BF_4$, possesses a *syn*-facial (*cisoid*) conformation of $M(CO)_3$ moieties, due to the formation of strong attractive intermolecular π(CO)–π(CO) interactions with a perpendicular packing motif (Tamm *et al.*, 2000). The conformation of $(CO)_3M(C_5H_4)$ moieties thus appears to depend, at least in part, on the type of π(CO)–π(CO) interactions formed.

The molecules in all four structures form zigzag chains due to the formation of strong attractive interactions. For (I) and (III), the zigzag chains along the crystallographic *b* axis involve strong attractive I···O interactions [$I1\cdots O2A(2 - x, -\frac{1}{2} + y, \frac{3}{2} - z) = 3.233$ (2) Å and $I1\cdots O2A-C7A = 112.1$ (2)° for (I), and $I1\cdots O2A(2 - x, -\frac{1}{2} + y, \frac{3}{2} - z) = 3.231$ (4) Å and $I1\cdots O2A-C7A$ 110.6 (3)° for (III)] (Fig. 5). The attractive nature of halogen–oxygen interactions is caused by electrostatic effects, polarization, charge transfer and dispersion contributions. The tendency to form short $X\cdots E$ (E = O and N) interactions (X = I > Br > Cl) increases with the magnitude of their polarizabilities (Lommerse *et al.*, 1996). The directionality of that type of interaction has been interpreted in terms of charge transfer between the highest occupied molecular orbital of E and the lowest unoccupied molecular orbital of X (Ramasubbu *et al.*, 1986). The strength of halogen–carbonyl interactions has been characterized as a function of two geometric parameters, the halogen–oxygen distance ($X\cdots O$) and the halogen–oxygen–carbon angle ($X\cdots O-C$). The interaction energy of the most strongly bound system was found to be 2.39 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) (iodobenzene–formaldehyde; $I\cdots O = 3.2$ Å and $I\cdots O-C = 110°$), of the same magnitude as those for $C-H\cdots O$ hydrogen bonds (Riley & Merz, 2007). The observed interactions in (I) and (III) are consistent in geometry with these calculated strong interactions.

According to a systematic CSD analysis (Allen *et al.*, 1998) of interactions between ketonic ($C_2-C{=}O$) carbonyl groups, three types of interaction motifs were identified: a predominant slightly sheared antiparallel motif, a perpendicular motif, and a highly sheared parallel motif. For transition metal carbonyls, a higher percentage of the perpendicular motif has been reported (Allen *et al.*, 2006). Compounds (II) and (IV) contain strong attractive antiparallel intermolecular π(CO)–

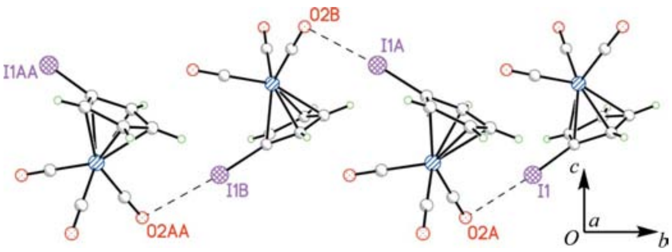

Figure 5
The zigzag chains formed along the b axis for (I). Dashed lines indicate the I$\cdots$O interactions. [Symmetry codes: (A) $-x + 2, y - \frac{1}{2}, -z + \frac{3}{2}$; (B) $x, y - 1, z$; (AA) $-x + 2, y - \frac{3}{2}, z + \frac{3}{2}$.]

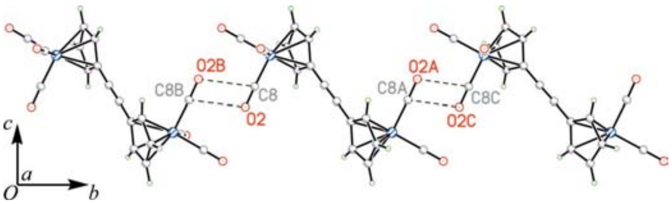

Figure 6
The zigzag chains formed along the b axis for (II). Dashed lines indicate the π(CO)–π(CO) interactions. [Symmetry codes: (A) $-x + 2, -y, z$; (B) $-x + 2, -y, -z$; (C) $x, y + 1, z$.]

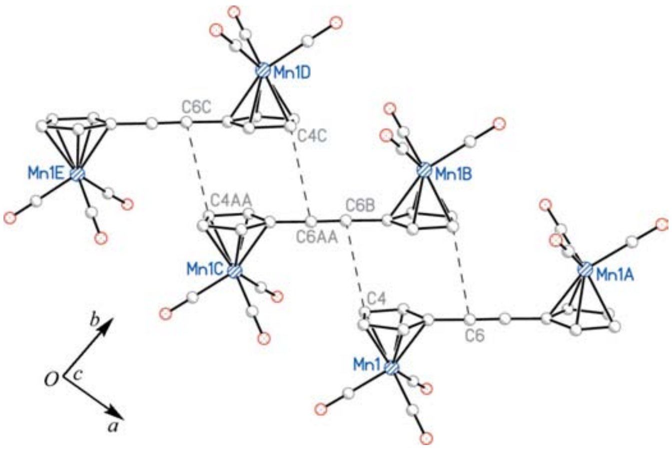

Figure 7
The $\pi(Csp^2)$–$\pi(Csp)$ stacking interactions (dashed lines) between pairs of molecules in (II). [Symmetry codes: (A) $-x + 2, -y + 1, -z$; (B) $-x + 1, -y + 1, -z$; (C) $x - 1, y, z$; (D) $-x, -y + 1, -z$; (E) $x - 2, y, z$; (AA) $x - 1, y, z$.]

π(CO) interactions between the carbonyl groups of neighboring molecules [O2$\cdots$C8A($2 - x, -y, z$) = 3.138 (2) Å, C8—O2$\cdots$C8A = 105.00 (10)° for (II), and O2$\cdots$C8A($2 - x, -y, z$) = 3.211 (6) Å and C8—O2$\cdots$C8A = 101.8 (3)° for (IV)], forming pairwise interactions in a sheared antiparallel dimer motif along the crystallographic b axis (Fig. 6). These antiparallel π(CO)–π(CO) interactions are a driving force for the formation of zigzag chains along the b axis. Comparison of the parameters obtained for (II) and (IV) with distances and angles reported for similar interactions in other transition metal carbonyls (2.95–3.60 Å/80–135°) indicates that the π(CO)–π(CO) interactions are relatively strong in (II) and (IV) (Allen *et al.*, 2006). Also, intermolecular π(CO)–π(CO) interactions are not rare, and sheared antiparallel and perpendicular motifs can be found for 14 of the 89 hits for monosubstituted cymantrenes and for 3 of the 27 hits for (η^5-C_5H_4X)Re(CO)$_3$ compounds in the CSD search (see above). The mean van der Waals radii used to identify intermolecular interactions and contacts were taken as C = 1.53 Å, O = 1.42 Å and I = 2.04 Å (Bondi, 1964).

The zigzag chains in (II) and (IV) are bound to each other by weak $\pi(Csp^2)$–$\pi(Csp^2)$ and $\pi(Csp^2)$–$\pi(Csp)$ stacking interactions between pairs of inversion-related molecules (C$\cdots$C distances *ca* 3.4 Å), leading to a ladder-type packing (Fig. 7).

Experimental

Compounds (I)–(IV) were prepared according to the standard literature procedure of Sterzo *et al.* (1989). Crystals of (I) and (III) were obtained by slow evaporation of hexane solutions. Crystals of (II) and (IV) were grown by slow evaporation of chloroform solutions at room temperature.

Compound (I)

Crystal data

[Mn(C_5H_4I)(CO)$_3$]
M_r = 329.95
Orthorhombic, $P2_12_12_1$
a = 7.2696 (5) Å
b = 10.7776 (7) Å
c = 12.0288 (8) Å

V = 942.44 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 4.64 mm^{-1}
T = 100 K
0.20 × 0.15 × 0.07 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.427, T_{max} = 0.717

9507 measured reflections
2278 independent reflections
2161 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.048
S = 1.06
2278 reflections
118 parameters
H-atom parameters constrained

$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}
Absolute structure: Flack (1983), with 948 Friedel pairs
Flack parameter: 0.05 (3)

Compound (II)

Crystal data

[$Mn_2(C_{12}H_8)$(CO)$_6$]
M_r = 430.12
Monoclinic, $P2_1/c$
a = 6.4096 (10) Å
b = 10.9991 (16) Å
c = 11.9798 (18) Å
β = 100.507 (2)°

V = 830.4 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.55 mm^{-1}
T = 100 K
0.31 × 0.11 × 0.10 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.645, T_{max} = 0.860

12974 measured reflections
2552 independent reflections
2211 reflections with $I > 2\sigma(I)$
R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.071$
$S = 1.05$
2552 reflections

118 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Compound (**III**)

Crystal data

$[Re(C_5H_4I)(CO)_3]$
$M_r = 461.21$
Orthorhombic, $P2_12_12_1$
$a = 7.4117$ (14) Å
$b = 10.922$ (2) Å
$c = 11.987$ (2) Å

$V = 970.3$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 15.67$ mm^{-1}
$T = 100$ K
0.14 × 0.10 × 0.07 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.218$, $T_{\max} = 0.407$

9533 measured reflections
2342 independent reflections
2276 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.041$
$S = 0.99$
2342 reflections
118 parameters
H-atom parameters constrained

$\Delta\rho_{\max} = 1.60$ e Å^{-3}
$\Delta\rho_{\min} = -1.39$ e Å^{-3}
Absolute structure: Flack (1983), with 970 Friedel pairs
Flack parameter: 0.015 (7)

Compound (**IV**)

Crystal data

$[Re_2(C_{12}H_8)(CO)_6]$
$M_r = 692.64$
Monoclinic, $P2_1/c$
$a = 6.2633$ (10) Å
$b = 11.7262$ (18) Å
$c = 11.8471$ (18) Å
$\beta = 98.206$ (2)°

$V = 861.2$ (2) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 14.08$ mm^{-1}
$T = 100$ K
0.20 × 0.11 × 0.09 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.165$, $T_{\max} = 0.364$

8399 measured reflections
2068 independent reflections
1817 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.051$
$S = 1.02$
2068 reflections

118 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 1.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.80$ e Å^{-3}

All H atoms were positioned geometrically, with C—H = 1.00 Å, and included in riding mode, with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$.

For all compounds, data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Table 1
Mean values of selected geometric parameters (Å, °) for (I), (II), (III) and (IV), and from the Cambridge Structural Database (CSD; Allen, 2002).

Cp′ is the C_5H_4X ring, M is Mn or Re, and $Cg1$ is the centroid of the C_5H_4X ring.

Parameter	(I)	(II)	CSD (M = Mn)
C—C for Cp′	1.417 (5)	1.425 (2)	1.415
M—C for Cp′	2.144 (3)	2.152 (2)	2.138
M—C(O)	1.796 (3)	1.800 (2)	1.790
C—O	1.153 (4)	1.149 (2)	1.148
$M1\cdots Cg1$	1.773 (2)	1.777 (1)	1.771
(O)C—M—C(O)	91.78 (15)	91.79 (6)	91.94
M—C—O	178.6 (3)	178.84 (13)	178.2

Parameter	(III)	(IV)	CSD (M = Re)
C—C for Cp′	1.423 (8)	1.423 (6)	1.419
M—C for Cp′	2.297 (5)	2.307 (5)	2.299
M—C(O)	1.912 (5)	1.907 (5)	1.902
C—O	1.145 (6)	1.157 (6)	1.156
$M1\cdots Cg1$	1.952 (2)	1.964 (2)	1.957
(O)C—M—C(O)	89.6 (2)	89.2 (2)	89.8
M—C—O	177.6 (5)	178.0 (4)	177.1

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3211). Services for accessing these data are described at the back of the journal.

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