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Crystal Structure of the Double Salt $(H_3\,tacn)$ *trans*-$[Ir(H_2O)_4\,Cl_2](SO_4)_2$ (tacn = 1,4,7-triazacyclononane)

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The *trans*-tetraaquadichloroiridium(III) ion, *trans*-$[Ir(H_2O)_4\,Cl_2]^+$, was found as a minor product (ca. 5%) in the reaction between $[Ir(H_2O)_6]^{3+}$ and tacn · 3HCl (tacn = 1,4,7-triazacyclononane) in an aqueous $Cs_2(SO_4)$ medium. The complex *trans*-$[Ir(H_2O)_4Cl_2]^+$ crystallizes as a double salt with $H_3\,tacn^{3+}$ and SO_4^{2-}. The crystal structure of $(H_3\,tacn)$*trans*-$[Ir(H_2O)_4\,Cl_2](SO_4)_2$ was determined by single-crystal X-ray diffraction [monoclinic, $C2/c$, $a = 11.8667(14)$, $b = 8.1145(11)$, $c = 19.319(3)$ Å, $\beta = 92.812(11)°$, $Z = 4$]. The concentration acid dissociation constants (25°C, 1.00 M $NaClO_4$) of *trans*-$[Ir(H_2O)_4\,Cl_2]^+$ were determined [$pK_1 = 6.31(2)$ and $pK_2 = 8.08(3)$].

The corresponding Cr(III) compound was also synthesized.

The preparation and studies of both aquation and anation of $[Ir(H_2O)_{6-x}\,Cl_x]^{3-x}$ and of $[Rh(H_2O)_{6-x}\,Cl_x]^{3-x}$ have been thoroughly investigated.[1–6] For the rhodium series[5,6] all representatives of the formula $[Rh(H_2O)_{6-x}\,Cl_x]^{3-x}$ have been prepared, and this is also the case for the corresponding iridium complexes,[1–4] although some of these are less well documented. However, only a few complexes ($x = 0$, 5, 6) have been isolated in solids.

In this paper we report the crystal structure and the electronic absorption spectrum of the *trans*-$[Ir(H_2O)_4\,Cl_2]^+$ ion. This ion was found in a double salt with the triply protonated 1,4,7-triazacyclononane cation ($H_3\,tacn^{3+}$) and SO_4^{2-} anions in a reddish precipitate, $(H_3\,tacn)$ *trans*-$[Ir(H_2O)_4\,Cl_2](SO_4)_2$, after the reaction between tacn · 3HCl and $Cs[Ir(H_2O)_6](SO_4)_2 \cdot 6H_2O$.[7]

The same type of salt could also be isolated with the *trans*-dichlorotetraaquachromium(III) complex as starting material. The chromium(III) compound was found to be isomorphous with the iridium(III) compound reported here.

Results and discussion

The reddish precipitate that was obtained as a by-product from the preparation of *fac*-$[Ir(tacn)\,Cl_3]$[7] was analyzed as tacn : SO_4^{2-} : Cl^- : Ir = 1 : 2 : 2 : ≈1. Since this was difficult to interpret, a structural study was performed. The single-crystal X-ray analysis showed that the compound was a double salt with the cations *trans*-$[Ir(H_2O)_4\,Cl_2]^+$ and $H_3\,tacn^{3+}$ (both on special crystallographic positions) and with SO_4^{2-} anions, and not a complex with tacn coordinated to Ir(III). This was a surprise, since tacn is known readily to form very stable complexes with both main group and transition metals.[8] However, this may be a consequence of the extreme substitution inertness of iridium(III).[4]

The structure of $(H_3\,tacn)$ *trans*-$[Ir(H_2O)_4\,Cl_2](SO_4)_2$ is depicted in Fig. 1, showing the different ions in the structure and the labelling of the atoms, and in Fig. 2, illustrating the crystal packing and the hydrogen-bonding pattern. The structure, as seen in Fig. 2, consists of alternating layers of (a) *trans*-$[Ir(H_2O)_4\,Cl_2]^+$ ions with the coordinated water molecules in the plane of the layer; (b) SO_4^{2-} ions; (c) $H_3\,tacn^{3+}$ ions oriented almost perpendicular relative to the layers; and finally (d) SO_4^{2-} ions. The Ir–Ir distances of neighbouring complex ions within the plane are 7.2 and 8.1 Å, respectively, while the shortest Ir–Ir distance between complexes in adjacent layers is 10.5 Å. Viewed in a different direction the $H_3\,tacn^{3+}$ ions form channels, with the ring systems stacked approximately 12 Å from each other. The sulfate ions form hydrogen bonds with all the coordinated water hydrogen atoms and with all amine protons of the triply protonated tacn. This extensive hydrogen bonding seems to be responsible for many of the interesting features seen in this structure, e.g. the crystal packing and the deviation from octahedral geometry of the iridium complex (described below). Bond lengths, angles and hydrogen-bonding distances are given in Tables 1, 2 and 3, respec-

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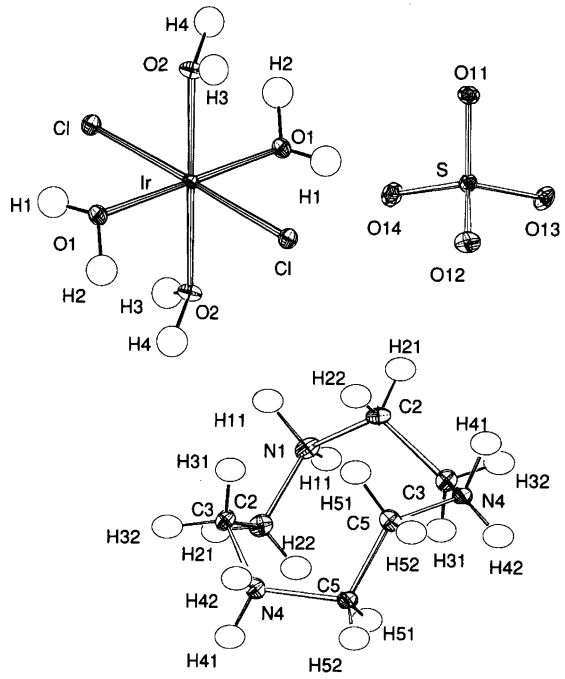

Fig. 1. ORTEP drawings of the different ions in $(H_3\,tacn)$-*trans*-$[Ir(H_2O)_4Cl_2](SO_4)_2$.

tively. The Ir–O bond lengths (average 2.04 Å) and Ir–Cl bond lengths (2.35 Å) are very close to those found in other Ir(III) complexes.[7,9] The coordination geometry around the iridium atom is distorted octahedral, with the *trans* Cl–Ir–Cl′, O1–Ir–O1′ and O2–Ir–O2′ angles at 180° (fixed by the crystallographic symmetry), the *cis* O–Ir–Cl angles around 90° but with two sets of *cis* O–Ir–O angles (one at 95.2° and one at 84.8°).

It was also possible to prepare the same kind of double salt using *trans*-$[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$ as starting material. The X-ray diffraction powder diagrams of the chromium(III) compound showed patterns similar to

Table 1. Interatomic distances (in Å).[a]

Ir–Cl	2.3502(7)	C2–C3	1.528(3)
Ir–O1	2.0390(13)	C2–H21	0.97(5)
Ir–O2	2.0484(14)	C2–H22	0.89(5)
O1–H1	0.79(4)	C3–N4	1.499(2)
O1–H2	0.93(5)	C3–H31	0.91(7)
O2–H3	0.75(4)	C3–H32	0.95(6)
O2–H4	1.02(5)	N4–C5	1.496(2)
S–O11	1.4984(15)	N4–H41	0.96(4)
S–O12	1.4758(14)	N4–H42	0.86(4)
S–O13	1.4720(15)	C5–C5′	1.528(4)
S–O14	1.471(2)	C5–H51	0.96(4)
N1–C2	1.502(2)	C5–H52	0.88(5)
N1–H11	0.99(4)		

[a] Symmetry operations: (′) $-x, y, -z-\frac{1}{2}$.

that of the iridium(III) compound, and it is therefore most likely that the compounds are isomorphous.

The electronic absorption spectrum of *trans*-$[Ir(H_2O)_4Cl_2]^+$ (Fig. 3), which is the first published spectrum of this ion, shows three d–d bands. The weak band at 500 nm ($\varepsilon = 7\ M^{-1}\,cm^{-1}$) is assigned as a triplet transition, and the bands at 362 nm ($\varepsilon = 50\ M^{-1}\,cm^{-1}$) and 300 nm ($\varepsilon = 44\ M^{-1}\,cm^{-1}$) are assigned as transitions to the split components $^1A_{1g} \rightarrow {}^1E_g\ (D_{4h})$ of the first excited singlet, $^1A_{1g} \rightarrow {}^1T_{1g}\ (O_h)$, and $^1A_{1g} \rightarrow {}^1B_{2g}\ (D_{4h})$ of the second excited singlet $^1A_{1g} \rightarrow {}^1T_{2g}\ (O_h)$, respectively.[10]

The concentration acidity constants (25.0°C, 1.00 M $NaClO_4$) of $(H_3\,tacn)$ *trans*-$[Ir(H_2O)_4Cl_2](SO_4)_2$ were determined by regression analysis of titration data as described by Mønsted and Mønsted.[11] The analysis showed three acid dissociation constants [$pK_1 = 6.31(2)$, $pK_2 = 7.40(2)$ and $pK_3 = 8.08(3)$]. A similar analysis of titration data of tacn · 3HCl showed only one acid dissociation constant [$pK = 7.37(1)$] in the range $2 < pK < 10$, as found by others (Ref. 8 and references therein). On this basis the two acid dissociation constants [$pK_1 = 6.31(2)$ and $pK_2 = 8.08(3)$] were assigned to the *trans*-$[Ir(H_2O)_4Cl_2]^+$ ion.

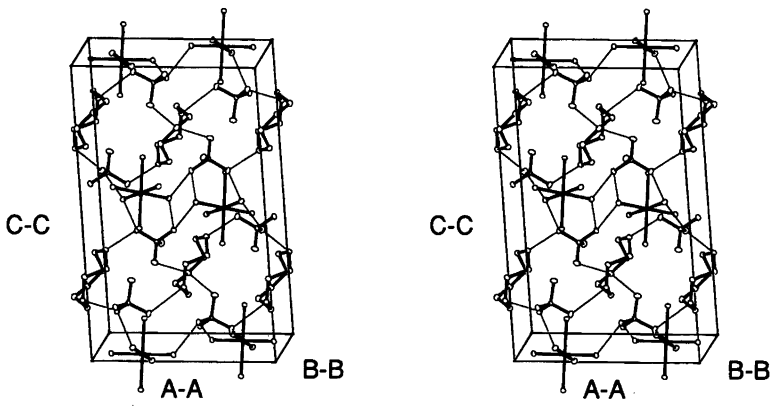

Fig. 2. Stereoscopic ORTEP drawing of the unit cell of $(H_3\,tacn)$*trans*-$[Ir(H_2O)_4Cl_2](SO_4)_2$.

Table 2. Bond angles (in °).[a]

O1–Ir–O1′	180.0	O14–S–O12	109.66(9)
O1–Ir–O2	95.24(6)	O13–S–O12	108.63(9)
O1–Ir–O2′	84.76(6)	O14–S–O11	107.95(9)
O2–Ir–O2′	180.0	O13–S–O11	109.57(9)
O1–Ir–Cl	88.44(4)	O12–S–O11	109.73(9)
O1–Ir–Cl′	91.56(4)	C2–N1–C2″	120.1(2)
O2–Ir–Cl	89.15(4)	N1–C2–C3	113.59(14)
O2–Ir–Cl′	90.85(4)	N4–C3–C2	113.01(14)
Cl–Ir–Cl′	180.0	C5–N4–C3	118.03(14)
O14–S–O13	111.28(9)	N4–C5–C5″	112.1(2)

[a] Symmetry operations: (′) $\frac{1}{2}-x, \frac{3}{2}-y, -z$; (″) $-x, y, -z-\frac{1}{2}$.

Experimental

Materials. 1,4,7-triazacyclononane trihydrochloride (tacn · 3HCl) was prepared as described in the literature.[12] All other chemicals were of analytical or reagent grade and were used without further purification.

Instrumentation. The absorption spectrum was recorded on a Perkin-Elmer Lambda 17 spectrophotometer. X-Ray powder diffraction photographs were taken with a Hägg–Guinier focusing camera (model XDC 700) calibrated with silicon and using Cu K_α radiation. Single-crystal data were collected with an Enraf–Nonius CAD4 diffractometer. The [H^+] measurements were carried out using a Radiometer PHM52 digital pH-meter equipped with a G202C glass electrode and a K401 calomel electrode, also from Radiometer. In the latter electrode the initial saturated potassium chloride solution was replaced with 1.0 M sodium chloride solution.

Analyses. C, H, N, Cl, Cr and S analyses were made by the Microanalytic Laboratory at the H. C. Ørsted Institute, Copenhagen.

Synthetic procedures.

*(H_3 tacn)*trans-*[$Ir(H_2O)_4Cl_2$](SO_4)$_2$*. This compound was formed when the mother liquor from the preparation of *fac*-[Ir(tacn)Cl_3][7] was left for evaporation for a few days. A small amount of a reddish solid was formed and isolated. The solid was recrystallized from hot water. The crystals were filtered off, washed with ethanol and diethyl ether and dried in air. These crystals were used in the structure determination. Anal. Found: C 11.1%, H 4.0%, N 6.4%, Cl 10.8%, S 9.6%. Calc. for $C_6H_{26}N_3Cl_2IrS_2O_{12}$: C 10.93%, H 3.97%, N 6.37%, Cl 10.75%, S 9.72%.

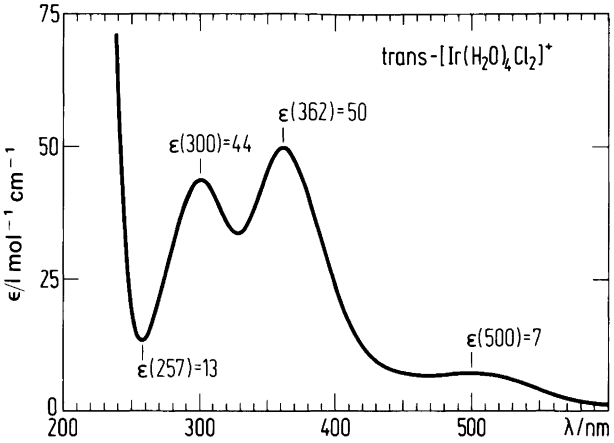

Fig. 3. Electronic spectrum of (H_3 tacn)*trans*-[$Ir(H_2O)_4Cl_2$](SO_4)$_2$ in H_2O.

*(H_3 tacn)*trans-*[$Cr(H_2O)_4Cl_2$]($SO_4$2*. A portion of tacn · 3HCl (0.1 g, 0.42 mmol) was dissolved in 5 ml water and [$Cr(H_2O)_4Cl_2$]Cl · $2H_2O$ (0.1 g, 0.38 mmol) was added. After addition of 5 drops of 2 M H_2SO_4 (0.25 ml, 0.5 mmol) light-green crystals started to precipitate, and the crystallization was completed by cooling in ice. The crystals were filtered off, washed with ethanol and diethyl ether, and dried in air. Yield 0.08 g (37%). Anal. Found: C 13.9, H 4.9%, N 7.8%, Cl 14.6%, S 12.4%, Cr 10.0%. Calc. for $C_6H_{26}N_3Cl_2CrS_2O_{12}$: C 13.88%, H 5.05%, N 8.09%, Cl 13.65%, S 12.35%, Cr 10.01%.

*Crystal structure determination of (H_3 tacn)*trans-*[$Ir(H_2O)_4Cl_2$](SO_4)$_2$*. A summary of the crystallographic data is given in Table 4. Diffraction data were collected for a tabular red crystal with dimensions

Table 3. Hydrogen bonding distances (in Å, D = donor and A = acceptor) and angles (in °).[a]

D–H···A		D···A	D–H	H···A	D···H···A
O1–H1···O11	(2)	2.622(2)	0.79(4)	1.87(5)	161(4)
O1–H2···O11	(3)	2.637(2)	0.93(5)	1.72(5)	169(4)
O2–H3···O13	(3)	2.698(2)	0.75(4)	1.97(4)	165(5)
O2–H4···O12	(4)	2.602(2)	1.02(5)	1.60(5)	166(4)
N1–H11···O14	(5)	2.778(2)	0.99(4)	1.82(5)	161(4)
N4–H41···O12	(1)	2.828(2)	0.96(4)	1.97(4)	147(4)
N4–H41···O13	(2)	2.750(2)	0.86(4)	1.93(4)	158(4)

[a] Symmetry operations: (1) x, y, z; (2) $x-\frac{1}{2}, y+\frac{1}{2}, z$; (3) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z$; (4) $x, y+1, z$; (5) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

Table 4. Crystallographic data.

Formula	$C_6H_{26}N_3Cl_2O_{12}S_2Ir$
Formula weight/g mol^{-1}	659.52
Space group	Monoclinic, $C2/c$ (No. 15)
Temperature/K	122
a/Å	11.8667(14)
b/Å	8.1145(11)
c/Å	19.319(3)
β/°	92.812(11)
V/Å^3	1858.0(4)
Z	4
D_c/g cm^{-3}	2.36
Radiation, λ (MoK_α)/Å	0.710 73
Abs. coeff., μ/cm^{-1}	77.28
Absorption: numerical	$T_{min}=0.221$, $T_{max}=0.571$
Max 2Θ/°	96
Total no. of reflections	8856
No. of unique data [$I>2\sigma(I)$]	6246
R	0.026
R_{w2}	0.075

0.36 × 0.34 × 0.19 mm. Three reflections were measured every 2.8 h to check for crystal decay. A linear decrease was observed during the data collection period to a total of 12.5%. 11 558 individual reflections were measured. The data reduction, performed with the DREADD[13] programs, included corrections for decay, Lorentz effects, polarization effects and absorption. For the latter correction the numerical program ABSORB[14] was used. Symmetry-related reflections were averaged, giving 8856 unique reflections ($R_{int}=0.03$). The structure was solved using SHELXS-86,[15] and refined with SHELXL-92.[16] Atomic scattering factors were taken from Refs. 17 and 18. In the least-squares refinement, which included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms, and an extinction parameter, to a total of 160 parameters, $\Sigma w(F_o^2-F_c^2)^2$ was minimized, where $w^{-1}=\sigma^2(F_o^2)+(0.0194P)^2+3.960P$ and $P=(F_o^2+2F_c^2)/3$. After the final refinement cycle the agreement factors were $R=0.026$ ($R=\Sigma\,|F_o-F_c|/\Sigma F_o$) for 6246 $F_o>4\sigma(F_o)$, $R_{w2}=0.075$ ($R_{w2}=[\Sigma\{w(F_o^2-F_c^2)\}^2/\Sigma\{wF_o^2\}^2]^{1/2}$), and $S=1.061$, and the maximum shift was -0.06σ. A final difference synthesis gave the highest and lowest residuals as 4.58 and −6.12 e Å^{-3}, respectively; as expected they were located around Ir. Atomic coordinates and thermal parameters are listed in Table 5. Tables of anisotropic thermal parameters and a listing of observed and calculated structure factors are available from the authors on request.

Table 5. Final positional and thermal parameters (in Å^2).[a]

Atom	x/a	y/b	z/c	U_{eq}/U_{iso}[b]
Ir	0.2500	0.7500	0.0000	0.00675(3)
Cl	0.27267(3)	0.74492(6)	0.12152(2)	0.01098(12)
O1	0.09016(11)	0.8360(2)	0.01000(7)	0.0115(4)
O2	0.32401(12)	0.9781(2)	0.00027(7)	0.0117(5)
S	0.36543(4)	0.29314(6)	−0.12127(2)	0.00854(12)
O11	0.45016(11)	0.4166(2)	−0.09371(7)	0.0118(4)
O12	0.26034(11)	0.3087(2)	−0.08399(8)	0.0140(4)
O13	0.41040(12)	0.1255(2)	−0.11050(8)	0.0131(5)
O14	0.34229(14)	0.3277(2)	−0.19534(7)	0.0160(6)
N1	0.0000	0.0378(3)	−0.2500	0.0133(8)
C2	0.0843(2)	0.1302(2)	−0.20430(10)	0.0133(6)
C3	0.03059(15)	0.2524(2)	−0.15555(9)	0.0118(5)
N4	0.07143(13)	0.4256(2)	−0.16440(8)	0.0111(5)
C5	0.06094(15)	0.5000(2)	−0.23527(10)	0.0119(5)
H1	0.059(4)	0.850(6)	−0.026(2)	0.035*
H2	0.086(4)	0.924(6)	0.041(2)	0.035*
H3	0.339(4)	1.012(6)	−0.034(2)	0.035*
H4	0.280(4)	1.061(6)	0.028(2)	0.035*
H11	−0.045(4)	−0.038(6)	−0.222(2)	0.040*
H21	0.124(4)	0.045(6)	−0.178(2)	0.040*
H22	0.132(4)	0.177(7)	−0.233(2)	0.040*
H31	−0.046(6)	0.251(4)	−0.155(4)	0.036*
H32	0.049(5)	0.229(5)	−0.108(3)	0.036*
H41	0.149(4)	0.416(6)	−0.148(2)	0.033*
H42	0.033(4)	0.488(5)	−0.138(2)	0.033*
H51	0.113(4)	0.442(6)	−0.263(2)	0.036*
H52	0.082(4)	0.604(6)	−0.230(2)	0.036*

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as:

$$U_{eq}=1/3\sum U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$$

[b] U_{iso} for the starred atoms were calculated as three times U_{eq} for the corresponding heavy atom.

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References

1. Poulsen, I. A. and Garner, C. S. *J. Am. Chem. Soc. 84* (1962) 2032.
2. El-Awady, A. A., Bounsall, E. J. and Garner, C. S. *Inorg. Chem. 6* (1967) 79.
3. Preetz, W. and Blasius, E. *Z. Anorg. Allg. Chem. 335* (1965) 1.
4. Castillo-Blum, S. E., Sykes, A. G. and Gamsjäger, H. *Polyhedron 6* (1987) 101.
5. Wolsey, W. C., Reynolds, C. A. and Kleinberg, J. *Inorg. Chem. 2* (1963) 463.
6. Palmer, D. A. and Harris, G. M. *Inorg. Chem. 14* (1975) 1316.
7. Gajhede, M., Simonsen, K. and Skov, L. K. *Acta Chem. Scand. 47* (1993) 271.
8. Chaudhuri, P. and Wieghardt, K. *Progr. Inorg. Chem. 35* (1987) 329.
9. Armstrong, R. S., Beattie, J. K. and Best, S. P. *J. Chem. Soc., Dalton Trans.* (1983) 1973.
10. Galsbøl, F. and Rasmussen, B. S. *Acta Chem. Scand., Ser. A 36* (1982) 439.
11. Mønsted, L. and Mønsted, O. *Acta Chem. Scand., Ser. A 30* (1976) 203.
12. Searle, G. H. and Geue, R. J. *Aust. J. Chem. 37* (1984) 959.
13. Blessing, R. H. *Crystallogr. Rev. 1* (1987) 3.
14. DeTitta, G. T. *J. Appl. Crystallogr. 18* (1985) 75.
15. Sheldrick, G. M. In: Sheldrick, G. M., Kruger, C. and Goddard, R., Eds., *Crystallographic Computing*, Oxford University Press 1985, Vol. 3, p. 175.
16. Sheldrick, G. M. *Prerelease of the program* (β-*version*).
17. Cromer, D. T. and Waber, J. T. In: *International Tables for X-Ray Crystallography*, The Kynoch Press, Birmingham 1974, Vol. IV, Table 2.2B.
18. Wilson, A. J. C. In: *International Tables for X-Ray Crystallography*, Kluwer Academic Publishers, Dordrecht, The Netherlands 1992, Vol. C, Tables 6.1.1.3, 4.2.6.8 and 4.2.4.2.

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