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Synthesis and characterization of Cu(I) chelate complexes with 1,3-bis(diphenylphosphino)propane, 1,2-bis(diphenylphosphino)benzene and perfluorinated carboxylates

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Abstract

Cu(I) complexes with 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(diphenylphosphino)benzene (dppB) and perfluorinated carboxylates of the general formula [Cu(diphosphine)$_2$](RCOO), R = C_2F_5, C_4F_9, C_6F_{13}, C_8F_{17}, C_9F_{19}, have been prepared and characterized with MS, IR and ^{1}H, ^{31}P, ^{13}C, ^{19}F, ^{63}Cu NMR spectroscopy. The presence of distinct bis-chelated cations of [Cu(diphosphine)$_2$]$^+$ type and uncoordinated carboxylate anions has been proposed.

Keywords: Copper(I); Diphosphines; Perfluorinated carboxylates; NMR; MS

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1. Introduction

The studies on transition metal complexes with diphosphines concerned mainly bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino) ethane (dppe) [1]. Some X-ray structures are also known for the coordination compounds of 1,3-bis(diphenylphosphino)propane (dppp) and 1,2-bis(diphenylphosphino)benzene (dppB) [2].

The two latter bidentate P-donor ligands reveal the preference for chelate coordination, due to the formation of six- and five-membered symmetric rings. The described species are neutral molecules of ML_2 or ML_2Cl_2 formula (L = dppp, dppB): [Pd^0(dppp)$_2$] [3], [Pt^0(dppp)$_2$] [4,5], *trans*-[Ru^{II}(dppp)$_2$Cl$_2$] [6], [Ni^0(dppB)$_2$] [7], *trans*-[Re^{II}(dppB)$_2$Cl$_2$] [8], *trans*-[Fe^{II}(dppB)$_2$Cl$_2$] · THF [9], *trans*-[Mo^{II}(dppB)$_2$Cl$_2$] [10] as well as ionic species containing complex cations of ML_2^{n+}, $ML_2Cl_2^{n+}$ or $ML_2O_2^{n+}$ type (L = dppp, dppB; $n = 1, 2$): [Ag^I(dppp)$_2$]$^+$SCN$^-$ · 1.5py [11], *trans*-[Re^V(dppp)$_2$O$_2$]$^+$(I$^-$, PF$_6^-$, ClO$_4^-$) · xH$_2$O · yCH$_3$OH [12,13], [Ni^{II}(dppB)$_2$]$^{2+}$(PF$_6^-$)$_2$ · C$_6$H$_5$CH$_3$ [14], *trans*-[Fe^{II}(dppB)$_2$(CH$_3$CN)$_2$]$^{2+}$(I$^-$)$_2$ [9]. The presence of ML_2^{n+} ions was also suggested, on the basis of spectroscopic methods, for [Au^I(dppp)$_2$]$^+$Cl$^-$ [15], [Ni^{II}(dppp)$_2$]$^{2+}$ (BF$_4^-$)$_2$ [14] and [Pd^{II}(dppp)$_2$]$^{2+}$(BF$_4^-$)$_2$ [14].

The chelate cation [Cu^I(dppp)$_2$]$^+$ was identified by X-ray structural studies in [Cu^I(dppp)$_2$]$^+$BF$_4^-$ [16] and [Cu^I(dppp)$_2$]$^+$ClO$_4^-$ · 0.5CH$_3$OH [17]. The Cu(I) atom possesses the distorted tetrahedral geometry with nearly equivalent Cu–P bonds (2.296–2.317 and 2.311–2.330 Å) and P–Cu–P bite angles much smaller than in an ideal tetrahedron (94°–98°). Similar structures consisting of [Cu^I(diphosphine)$_2$]$^+$ cations and uncoordinated inorganic anions were proposed for [Cu^I(dppp)$_2$]$^+$Cl$^-$ [18], [Cu^I(dppp)$_2$]$^+$I$^-$ [16], [Cu^I(dppp)$_2$]$^+$PF$_6^-$ [19] and [Cu^I(dppB)$_2$]$^+$PF$_6^-$ [19].

During the present work, we have synthesized two series of Cu(I) coordination compounds with dppp or dppB and perfluorocarboxylates, their general formula being [Cu(diphosphine)$_2$]$^+$RCOO$^-$, where R = C_2F_5, C_4F_9, C_6F_{13}, C_8F_{17}, C_9F_{19}. To the best of our knowledge, these are the first Cu(I)–dppp and dppB complexes with organic counterions. Recently, we have described such species for the ligand dppe [20]. As the carboxylates are potential O-donors, the possibility of their mono- or bidentate (bridging or chelating) coordination could not

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be excluded a priori. Such Cu(I) diphosphine–carboxylate complexes with metal-bonded $RCOO^-$ anions are known for dppm, e.g.: $[Cu^I_2(\mu\text{-dppm})_2(\mu\text{-}O_2CCH_3)]^+ BF_4^- \cdot (CH_3)_2CO$ [21].

We chose perfluorocarboxylic acids as auxiliary ligands in order to increase the complexes volatility, which was helpful in mass spectral measurements. A relatively good solubility in $CDCl_3$ allowed us to apply ^1H, ^{31}P, ^{13}C, ^{19}F and ^{63}Cu NMR spectroscopy. The IR spectra were also measured to determine the carboxylic anions' coordination mode.

2. Experimental

2.1. Materials

Cu powder (99.999%), RCOOH acids ($R = C_2F_5$, C_4F_9, C_6F_{13}, C_8F_{17}, C_9F_{19}; 97–99%), dppp (97%) and dppB (97%) were purchased from Aldrich, whereas $CuCO_3 \cdot Cu(OH)_2 \cdot nH_2O$ (99%) was from POCh Gliwice (Poland). CH_3CN and CH_2Cl_2 were supplied by POCh and Fluka, respectively, and dried by standard methods.

2.2. Methods

Mass spectra were detected at ambient temperature with an AMD-640 mass spectrometer, using LSIMS+ or FAB+ ionization methods for dppp and dppB complexes, respectively. Nitrobenzyl alcohol was used as a liquid matrix. NMR spectra were recorded with a Varian Gemini-XL 200 MHz spectrometer, using the following frequencies and standards: ^1H: 199.99 MHz, TMS; ^{13}C: 50.29 MHz, TMS; ^{19}F: 188.16 MHz, $CFCl_3$; ^{31}P: 80.96 MHz, 85% H_3PO_4; ^{63}Cu: 53.00 MHz, $[Cu(CH_3CN)_4]ClO_4$. The solvent was $CDCl_3$, the temperature 298 K, the sample concentration 0.02 M. IR spectra were measured in the 4000–400 cm^{-1} range with a Spectrum 2000 Perkin–Elmer FT-IR spectrometer, using KBr discs. The amount of Cu was determined with a Carl-Zeiss Jena AAS spectrophotometer, that of C, H by elemental microanalysis.

2.3. Synthesis

$Cu(RCOO)_2$ salts ($R = C_2F_5$, C_4F_9, C_6F_{13}, C_8F_{17}, C_9F_{19}) were obtained from $CuCO_3 \cdot Cu(OH)_2 \cdot nH_2O$ and RCOOH in water or water–ethanol (10:1) solution. $[Cu(dppp)_2](RCOO)$ and $[Cu(dppB)_2](RCOO)$ complexes were prepared as follows: $Cu(RCOO)_2$ (0.8 mmol in 20 cm^3 of CH_3CN) was placed in a Schlenk tube and an excess of Cu powder (8 mmol) was added. The obtained suspension was stirred under argon until it became colorless, then dppp or dppB (3.2 mmol in 20 cm^3 of CH_2Cl_2) was added. The reaction mixture was stirred for 12 h, filtered and evaporated on a vacuum line, giving yellow or colorless crystals. The yield was 73–91%. The results of elemental analyses are listed below (%; calc./found):

(**1**) $[Cu(dppp)_2](C_2F_5COO)$	$(C_{57}H_{52}CuF_5O_2P_4)$	C(65.1/64.8), H(5.0/5.2), Cu(6.0/6.0)
(**2**) $[Cu(dppp)_2](C_4F_9COO)$	$(C_{59}H_{52}CuF_9O_2P_4)$	C(61.5/61.2), H(4.8/5.1), Cu(5.5/5.6)
(**3**) $[Cu(dppp)_2](C_6F_{13}COO)$	$(C_{61}H_{52}CuF_{13}O_2P_4)$	C(58.5/58.4), H(4.2/4.5), Cu(5.1/5.2)
(**4**) $[Cu(dppp)_2](C_8F_{17}COO)$	$(C_{63}H_{52}CuF_{17}O_2P_4)$	C(56.0/56.3), H(3.9/4.1), Cu(4.7/4.9)
(**5**) $[Cu(dppB)_2](C_2F_5COO)$	$(C_{63}H_{48}CuF_5O_2P_4)$	C(67.6/67.6), H(4.3/4.2), Cu(5.7/5.4)
(**6**) $[Cu(dppB)_2](C_4F_9COO)$	$(C_{65}H_{48}CuF_9O_2P_4)$	C(64.0/64.0), H(4.0/3.9), Cu(5.2/5.2)
(**7**) $[Cu(dppB)_2](C_6F_{13}COO)$	$(C_{67}H_{48}CuF_{13}O_2P_4)$	C(61.0/60.8), H(3.7/3.5), Cu(4.8/5.0)
(**8**) $[Cu(dppB)_2](C_8F_{17}COO)$	$(C_{69}H_{48}CuF_{17}O_2P_4)$	C(58.4/58.3), H(3.4/3.2), Cu(4.5/4.7)
(**9**) $[Cu(dppB)_2](C_9F_{19}COO)$	$(C_{70}H_{48}CuF_{19}O_2P_4)$	C(57.2/57.0), H(3.3/3.1), Cu(4.3/4.4)

3. Results and discussion

3.1. Mass spectrometry

The most intensive peaks and the proposed assignments are presented in Tables 1 and 2. The fragments containing one or two Cu atoms have appeared as two or three isotopic peaks with 1:0.45 or 1:0.9:0.2 intensity ratios, respectively (due to the natural abundance of ^{63}Cu and ^{65}Cu being 69.1 and 31.9%).

3.1.1. Dppp complexes **1**–**4**

The main signal (100%, 887 m/z) is always $[Cu(dppp)_2]^+$, whereas the intensity of $[Cu(dppp)_2(RCOO)]^+$ molecular peaks does not exceed 1%. It suggests that molecules **1**–**4** consist of distinct $[Cu(dppp)_2]^+$ and $RCOO^-$ ions. The other signals derive from mononuclear fragments $[Cu(dppp)]^+$ (34–78%), $[Cu(dppp)(RCOO)]^+$ (3–27%) and $[Cu(dppp)(Ph_2P)]^+$ (12–24%). The binuclear species, detected at 1113 (**1**), 1213 (**2**), 1313 (**3**) 1415 (**4**) m/z and 702 (**1**), 902 (**3**), 1001 (**4**) m/z, can be, respectively, assigned to $[Cu_2(dppp)_2(RCOO)]^+$ and $[Cu_2(dppp)(RCOO)]^+$, formed upon secondary recombination processes. Their formation and stability is evi-

Table 1
Characteristic fragments in the mass spectra of $[Cu(dppp)_2]RCOO$ complexes **1**–**4**

Fragment	1	2	3	4
$[Cu_2(dppp)_2(RCOO)]^+$	1113 (0.03%)	1213 (0.03%)	1313 (2%)	1415 (7%)
$[Cu(dppp)_2(RCOO)]^+$		1150 (0.04%)	1249 (1%)	1351 (1%)
$[Cu(dppp)_2]^+$	887 (100%)	887 (100%)	887 (100%)	887 (100%)
$[Cu_2 (dppp)(RCOO)]^+$	702 (3%)		902 (12%)	1003 (36%)
$[Cu(dppp)(RCOO)]^+$	638 (3%)	738 (4%)	838 (23%)	938 (27%)
$[Cu(dppp)]^+$	475 (34%)	475 (66%)	475 (78%)	475 (44%)

Table 2
Characteristic fragments served in the mass spectra of $[Cu(dppB)_2]RCOO$ complexes **5**–**9**

Fragment	5	6	7	8	9
$[Cu(dppB)_2R]^+$		1173 (4%)	1273 (2%)	1373 (4%)	1423 (6%)
$[Cu(dppB)_2]^+$	955 (45%)	955 (53%)	955 (76%)	955 (53%)	955 (58%)
$[Cu(dppB)]^+$	509 (76%)	509 (76%)	509 (81%)	509 (77%)	509 (79%)
$[P_2Ph_3Phen]^+$	369 (100%)	369 (100%)	369 (100%)	369 (100%)	369 (100%)
$[P_2PhPhen]^+$	214 (8%)	214 (8%)	214 (2%)	214 (3%)	
$[PPh_2]^+$	183 (59%)	183 (60%)	183 (63%)	183 (63%)	183 (63%)

Phen = C_6H_4.

dently more favored for longer carboxylates. Diphosphine fragmentation signals were observed also, with similar patterns to those reported for Cu(I) complexes with 1,2-bis(diphenylphosphino)ethane [20].

3.1.2. *DppB complexes* **5**–**9**

The hypothetical $[Cu(dppB)_2RCOO]^+$ molecular peaks are absent, contrary to those of $[Cu(dppB)_2R]^+$ (2–6%). The presence of $[Cu(dppB)_2R]^+$ peaks, in contrast to the lack of analogous $[Cu(dppp)_2R]^+$ signals in the mass spectra of **1**–**4**, can be explained by interaction between $[Cu(dppB)_2]^+$ and RCOO in the liquid matrix and by different properties of the "aliphatic" (dppp) and aromatic (dppB) diphosphine. The signals of $[Cu(dppB)_2]^+$ and $[Cu(dppB)]^+$ are much more intensive (45–76% and 76–81%), which indicates that **5**–**9** molecules contain chelate $[Cu(dppB)_2]^+$ cations. Oppositely to **1**–**4** compounds, no binuclear species have been detected. Some other fragments, derived from pure ligand are present: 369 *m/z* (100%, $[P_2Ph_3Phen]^+$); 183 *m/z* (59–63%, $[PPh_2]^+$); 446 *m/z* (4–11%, $dppB^+$); 214 *m/z* (2–8%, $[P_2PhPhen]^+$), the former appearing as the main peak in all spectra.

The proposed fragmentation schemes are presented in Figs. 1 and 2.

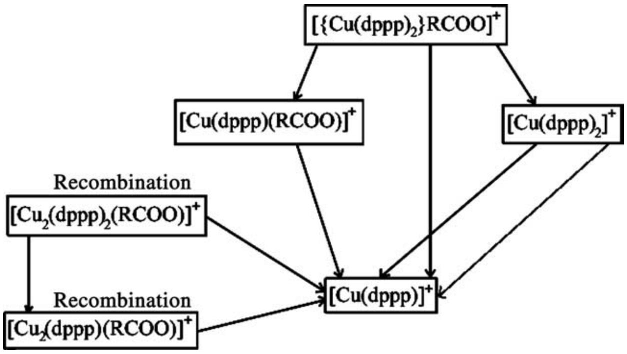

Fig. 1. The fragmentation scheme of $[Cu(dppp)_2]RCOO$ complexes **1**–**4**.

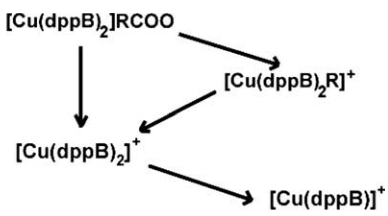

Fig. 2. The fragmentation scheme of $[Cu(dppp)_2]RCOO$ complexes **5**–**9**.

3.2. *IR spectroscopy*

The asymmetric and symmetric stretching vibrations modes of the carboxylic groups appear in the ranges $\nu_a(COO) = 1691$–1696 cm^{-1} and $\nu_s(COO) = 1434$–1436 cm^{-1}. These values are nearly identical with those found for the respective sodium salts: $\nu_a(COO) = 1696$–1698 cm^{-1} and $\nu_s(COO) = 1422$–1428 cm^{-1}, confirming the suggestion that $RCOO^-$ anions are uncoordinated [20]; of course some cation–anion interaction cannot be excluded.

3.3. *NMR spectroscopy*

3.3.1. *Dppp complexes* **1**–**4**

The ^1H signals of 2.30 and 1.70 ppm can be easily assigned to $CH_{2\alpha}$ and $CH_{2\beta}$ [22]. They are slightly shifted to higher frequency (less than 0.1 ppm), comparing to free dppp (2.23, 1.64 ppm).

Table 3
The ^{31}P and ^{13}C chemical shifts of dppp and **1**–**4** (coordination shifts in parentheses)

Compound	P	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	$CH_{2\alpha}$	$CH_{2\beta}$
Dppp	−16.8[a]	138.7[b]	132.7[b]	128.4[b]	128.3[b]	29.7[b]	22.6[b]
1	−8.6 (+8.2)	132.9 (−5.8)	132.0 (−0.7)	129.9 (+1.5)	128.5 (+0.2)	27.5 (−2.2)	17.3 (−5.3)
2	−9.3 (+7.5)	133.2 (−5.5)	132.3 (−0.4)	130.3 (+1.9)	128.8 (+0.5)	27.9 (−1.8)	17.6 (−5.0)
3	−8.7 (+8.1)	133.2 (−5.5)	132.3 (−0.4)	130.2 (+1.8)	128.8 (+0.5)	27.9 (−1.8)	17.7 (−4.9)
4	−8.9 (+7.9)	133.2 (−5.5)	132.3 (−0.4)	129.9 (+1.5)	128.5 (+0.2)	27.7 (−2.0)	17.7 (−4.9)

[a] ^{31}P literature data: from −17.2 to −17.8 ppm [15,16,22,26].

[b] ^{13}C literature data: $CH_{2\alpha}$ 29.6, $CH_{2\beta}$ 22.3, C_{ipso} 138.6, C_{orto} 132.6, C_{meta} 128.3 and C_{para} 128.4 ppm [26].

The ^{31}P and ^{13}C chemical shifts of dppp and **1**–**4** are listed in Table 3.

The ^{31}P NMR spectra reveal a singlet in the range from −8.6 to −9.3 ppm, shifted ca. 8 ppm to higher frequency in comparison to free dppp ($\delta = -16.8$). All phosphorus atoms remain magnetically equivalent which proves the chelate coordination mode of dppp molecules. Analogous results were already reported for $[Cu^{I}(dppp)_2]^+Cl^-$, $[Cu^{I}(dppp)_2]^+I^-$, $[Cu^{I}(dppp)_2]^+BF_4^-$ and $[Cu^{I}(dppp)_2]^+PF_6^-$ (δ being −13.1, −8.8, −8.5 and −10 ppm, respectively) [16,18,19]. The observed deshielding of ^{31}P nuclei seems to be typical for $[Cu(dppp)_2]^+$ chelate cations, confirming their presence in the studied complexes. However, the measured high-frequency coordination shifts are smaller than those found for $[Ag^{I}(dppp)_2]^+SCN^-$, $[Au^{I}(dppp)_2]^+Cl^-$, $[Ni^{II}(dppp)_2]^{2+}(BF_4^-)_2$ and $[Pd^{II}(dppp)_2]^{2+}(BF_4^-)_2$ (δ being −4.7, −2.7, −7.8 and 0.0 ppm, respectively) [11,14,15].

In the ^{13}C NMR spectra both C_{ipso} and $CH_{2\alpha}$, $CH_{2\beta}$ nuclei are shielded upon Cu(I) coordination, this effect being opposite to that noted for ^{31}P. The observed low-frequency shifts are ca. 5.5, 2 and 5 ppm, respectively, the $CH_{2\beta}$ signals being shifted more than $CH_{2\alpha}$. This phenomenon can be explained if it is assumed that in $[Cu(dppp)_2]^+$ chelate cations the CH_2 groups interact with Cu atoms along two bond chains. The cumulated influence of the Cu(I) moiety via three bonds in both directions ($CH_{2\beta}$) is more expressed than that via four and two bonds ($CH_{2\alpha}$).

The carboxylic groups are detected at ca. 160 ppm as sharp triplets (coupling with α-CF_2 groups), similar to those of the respective RCOOH acids, e.g., for **1** $\delta = 160.1$ ppm, for C_2F_5COOH $\delta = 163.4$ ppm. Also the ^{19}F NMR spectra are analogous, e.g., for **1** the β-CF_3 and α-CF_2 peaks appear at −4.6 and −41.4 ppm, whereas for C_2F_5COOH at −5.6 and −44.9 ppm, respectively. For **2**, **3** and **4** the β-CF_3 and α-CF_2 peaks are observed at −3.2 and −38.3 ppm; −3.1 and −38.0 ppm; −3.0 and −38.1 ppm, respectively. Neither for COO (^{13}C) nor α-CF_2 (^{19}F) signals is the quadrupolar broadening by ^{63}Cu or ^{65}Cu observed, excluding the possibility of direct binding of perfluorocarboxylic anions to Cu(I). The small chemical shift changes, comparing to RCOOH acids (the data for RCOONa salts not being available due to their insolubility in $CDCl_3$) can be regarded as a result of deprotonation.

The ^{63}Cu resonances appear as broad ($\nu_{1/2}$ ca. 8.5 kHz) bands at ca. 230 ppm, similar data being noted for $[Cu^{I}(dppp)_2]^+PF_6^-$ ($\delta = 231$ ppm and $\nu_{1/2} = 4$ kHz) [19]. The high values of ^{63}Cu half-line widths, comparing to the reference standard (440 Hz for $[Cu(CH_3CN)_4]^+ClO_4^-$ [23]), as well as the lack of ^{63}Cu–^{31}P couplings are the result of quadrupolar relaxation and suggest a low symmetry around the central atom. In ideally tetrahedral $[Cu(monophosphine)_4]^+Cl^-$ and $[Cu(monophosphite)_4]^+$ Cl^- complexes, possessing T_d microsymmetry, the ^{63}Cu nuclei were detected as relatively sharp signals with multiplet structures [24]. In fact, for the discussed bis-chelated $[Cu(dppp)_2]^+$ cations one can assume rather the lower, pseudotetrahedral C_{2v} geometry. The ^{31}P and ^{63}Cu temperature variable NMR experiments revealed no interesting phenomena upon decreasing the temperature, which excluded the occurrence of dynamic processes involving the $[Cu(dppp)_2]^+$ species.

3.3.2. DppB complexes **5**–**9**

The ^{1}H and ^{13}C NMR spectra are analogous to those of free dppB, their assignment and coordination shifts discussion being difficult due to overlapping of phenyl and phenylene resonances. The ^{19}F signals shift very slightly, e.g., for **5** the β-CF_3 and α-CF_2 groups appear at −6.2 and −43.1 ppm. For **6**, **7**, **8** and **9** the β-CF_3 and α-CF_2 peaks were detected at −4.8 and −40.3 ppm; −4.6 and −39.9 ppm; −4.6 and −39.9 ppm; −4.6 and −39.8 ppm, respectively. Hence the coordination shifts are between −0.6 and 0.3 ppm.

The ^{31}P NMR spectra reveal a singlet in the range from 8.3 to 8.6 ppm, shifted ca. 22 ppm to higher frequency comparing to free dppB, for which we have found $\delta = -12.7$ ppm (literature data being −13.3 ppm [25]). As in the case of compounds **1**–**4**, the equivalency of all phosphorus atoms can be regarded as the proof for bis-chelated coordination of Cu(I). It is worth noting that the deshielding effect is evidently larger for dppB than dppp complexes, this fact being already reported for $[Cu^{I}(dppB)_2]^+PF_6^-$ ($\delta = +9.0$ ppm) [19]. No dynamic processes were observed upon the decreasing temperature.

In the case of **5–9** compounds we have not been able to detect their ^{63}Cu NMR spectra, this problem also being reported for dppB complexes by other workers [19].

4. Conclusions

The MS, IR and NMR spectra suggest that the studied Cu(I) complexes with dppp or dppB and perfluorocarboxylates consist of distinct bis-chelated pseudotetrahedral $[Cu(diphosphine)_2]^+$ cations and uncoordinated $RCOO^-$ anions. The formation of Cu–P coordination bondings results in the high-frequency shifts of ^{31}P NMR signals, the observed deshielding effect being more expressed for dppB than dppp compounds.

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