

## New Copper(I) Perfluorinated Carboxylates Complexes with Bis(diphenylphosphine)methane

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Copper(I) perfluorinated carboxylates complexes with bis(diphenylphosphine)methane (dppm) of general formula  $[\text{Cu}_2(\mu\text{-dppm})_3(\text{RCOO})_2]\cdot\text{dppm}$ , where  $\text{R} = \text{C}_2\text{F}_5, \text{C}_4\text{F}_9, \text{C}_6\text{F}_{13}, \text{C}_8\text{F}_{17}, \text{C}_9\text{F}_{19}$ , have been prepared and characterized by vibrational,  $^{31}\text{P}$  CPMAS NMR and  $^{13}\text{C}$  CPTOSSB NMR mass spectra in the solid state.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  NMR and variable temperature  $^{31}\text{P}$  NMR spectra were measured in solution. Temperature variable  $^{31}\text{P}$  NMR spectra revealed at least three dimeric species in equilibrium. IR and mass spectra analyses suggest dimeric complexes with three bridging diphosphines and monodentate carboxylates in the solid state.

**Key words:** copper(I), diphosphine, perfluorinated carboxylates, multinuclear NMR, MS, IR

Bis(diphenylphosphine)methane (dppm) has been extensively used as a bridging ligand for transition metal complexes and many examples of bi-, tri- and tetranuclear dppm compounds of copper(I) are reported [1–5]. Dppm exhibits stronger  $\pi$ -acceptor properties than tertiary phosphines, what results in additional stabilization of Cu(I) complexes. However, when carboxylates are secondary ligands for Cu(I), the destabilization of the coordination sphere is observed. This feature can be related to the strong  $\sigma$ -donor properties of carboxylates. Moreover, Cu(I) perfluorinated carboxylates complexes are less stable than aliphatic analogues because oxygen atoms reveal lower  $\sigma$ -donor properties, causing further destabilization of Cu–O bond. The same feature was observed for copper(I) complexes with  $\beta$ -diketones, what can be explained by the hard-soft acids-bases theory [6]. On the other hand, copper(I) perfluorinated carboxylates can exist in many different geometries, depending on the secondary ligand in the coordination sphere [1,4,5]. Hence one may presume that copper(I) complexes with perfluorinated carboxylates will reveal new structures and properties. Besides that, in previous studies we have found that Ag(I) and Au(I) perfluorinated carboxylates complexes with tertiary phosphines are good CVD precursors for silver and gold [7]. This prompted us for synthesis of Cu(I) complexes with similar properties. Thus, the main purpose of this study was the preparation of new Cu(I) perfluorinated carboxylate complexes with dppm and their characterization by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  NMR in the solid state and in the solution, as well as by IR and MS spectroscopy.

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## EXPERIMENTAL

**Instrumentation:** Mass spectra were registered with an AMD-640 mass spectrometer, using LSIMS and FAB+ ionization method and NBA alcohol as a liquid matrix. NMR spectra were recorded with a VARIAN GEM 200 MHz at typical frequencies for  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$ . Standard for  $^1\text{H}$ ,  $^{13}\text{C}$  was TMS, whereas for  $^{19}\text{F}$  NMR  $\text{CFCl}_3$ .  $^{31}\text{P}$  NMR spectra were measured at 80.95 MHz using 85%  $\text{H}_3\text{PO}_4$  as a standard.  $\text{CDCl}_3$  served as solvent for all NMR measurements. Temperature-variable  $^{31}\text{P}$  and  $^{63}\text{Cu}$  NMR spectra were measured with a Bruker 300 MSL spectrometer in  $\text{CDCl}_3$ . Concentration of complexes was 0.02 mol/dm<sup>3</sup> and line width of the peaks were measured without baseline correction or apodization function in the data processing. Solid-state  $^{13}\text{C}$  NMR measurements were performed by Cross Polarization Total Sideband Suppression B (CPTOSSB) method, whereas  $^{31}\text{P}$  NMR with CPMAS. IR spectra were registered with a Spectrum 2000 Perkin Elmer FT-IR spectrometer in the range 4000–400 cm<sup>-1</sup> using KBr discs, whereas in 700–100 cm<sup>-1</sup> using polyethylene discs. Copper was determined on a Carl Zeiss Jena AAS spectrophotometer.

**Chemicals:** Perfluorinated carboxylic acids (97–99%) and bis(diphenylphosphine)methane were purchased from Aldrich and used without further purification. Acetonitrile and methylene chloride (Aldrich) were purified and dried by standard methods. Copper powder for organic synthesis from Aldrich and copper(II) carbonate from POCh Gliwice were used as received. Copper(II) carboxylates  $\text{Cu}(\text{RCOO})_2$ , where  $\text{R} = \text{C}_2\text{F}_5$ ,  $\text{C}_4\text{F}_9$ ,  $\text{C}_6\text{F}_{13}$ ,  $\text{C}_8\text{F}_{17}$ ,  $\text{C}_9\text{F}_{19}$ , were obtained in reaction of a slight excess of copper(II) carbonate with the respective perfluorinated carboxylic acid in water or water-ethanol (10:1) solution. The stoichiometry of the prepared salts was proved by the metal determination and IR spectra.

**Synthesis:** Complexes of the type  $[\text{Cu}_2(\mu\text{-dppm})_3(\text{RCOO})_2]\cdot\text{dppm}$ , where  $\text{R} = \text{C}_2\text{F}_5$ ,  $\text{C}_4\text{F}_9$ ,  $\text{C}_6\text{F}_{13}$ ,  $\text{C}_8\text{F}_{17}$ ,  $\text{C}_9\text{F}_{19}$ , were obtained according to the general procedure, in which copper(II) perfluorinated carboxylates (0.2 mmol) were placed in the Schlenk tube, dissolved in 20 cm<sup>3</sup> of fresh distilled acetonitrile and excess of the copper powder was added under argon (1.5 g, 24 mmol). The obtained suspension was stirred until solution became colourless. To the resulting solution, bis(diphenylphosphine)methane (0.8 mmol) in 20 cm<sup>3</sup> of methylene chloride was added, reaction mixture stirred for 12 h, filtered and evaporated on vacuum line, giving yellow or colourless crystals. Recrystallization from methylene chloride gave white solids. The results of elemental analyses confirmed the following compositions:

1.  $\text{C}_{106}\text{H}_{88}\text{P}_8\text{F}_{10}\text{O}_4\text{Cu}_2$ ; 2.  $\text{C}_{110}\text{H}_{88}\text{P}_8\text{F}_{18}\text{O}_4\text{Cu}_2$ ; 3.  $\text{C}_{114}\text{H}_{88}\text{P}_8\text{F}_{26}\text{O}_4\text{Cu}_2$ ; 4.  $\text{C}_{118}\text{H}_{88}\text{P}_8\text{F}_{34}\text{O}_4\text{Cu}_2$ ;
5.  $\text{C}_{120}\text{H}_{88}\text{P}_8\text{F}_{38}\text{O}_4\text{Cu}_2$ .

## RESULTS AND DISCUSSION

**Mass spectra analysis:** LSIMS spectrum of **1** dissolved in NBA liquid matrix is presented in Figure 1. The most pronounced peaks represent the following fragments:  $[\text{Cu}_2(\text{C}_2\text{F}_5\text{COO})_2(\text{dppm})_2]^+$  1221 (16%),  $[\text{Cu}_2(\text{C}_2\text{F}_5\text{COO})(\text{dppm})_2]^+$  1057 (52%),  $[\text{Cu}_2(\text{C}_2\text{F}_5\text{COO})(\text{dppm})]^+$  673 (68%) (Table 1). Besides the most abundant dimeric fragments also monomeric species were found, which can be related to the partial dimers dissociation processes. Observed trimeric fragments (4% and 1% intensity) (Table 1) exhibit the lowest population, what can be referred to the recombination processes of monomeric and dimeric species. Postulated dimeric species have further evidence in IR spectra [8,9] (*vide infra*). Similar fragmentation pattern was observed for complexes **2**, **3**, **4** and **5** (Table 1). The absence of the molecular peak can be caused by the reactions in the solvage, which are responsible for the formation, or at least a partition of fragment ions. Fragmentation process of bis(diphenylphosphine)methane has also resulted in many characteristic peaks (*i.e.* 384 m/z, 262 m/z, 199 m/z, 183 m/z, 121 m/z with intensity between 15 and 70%), what is in favor of the coordinated

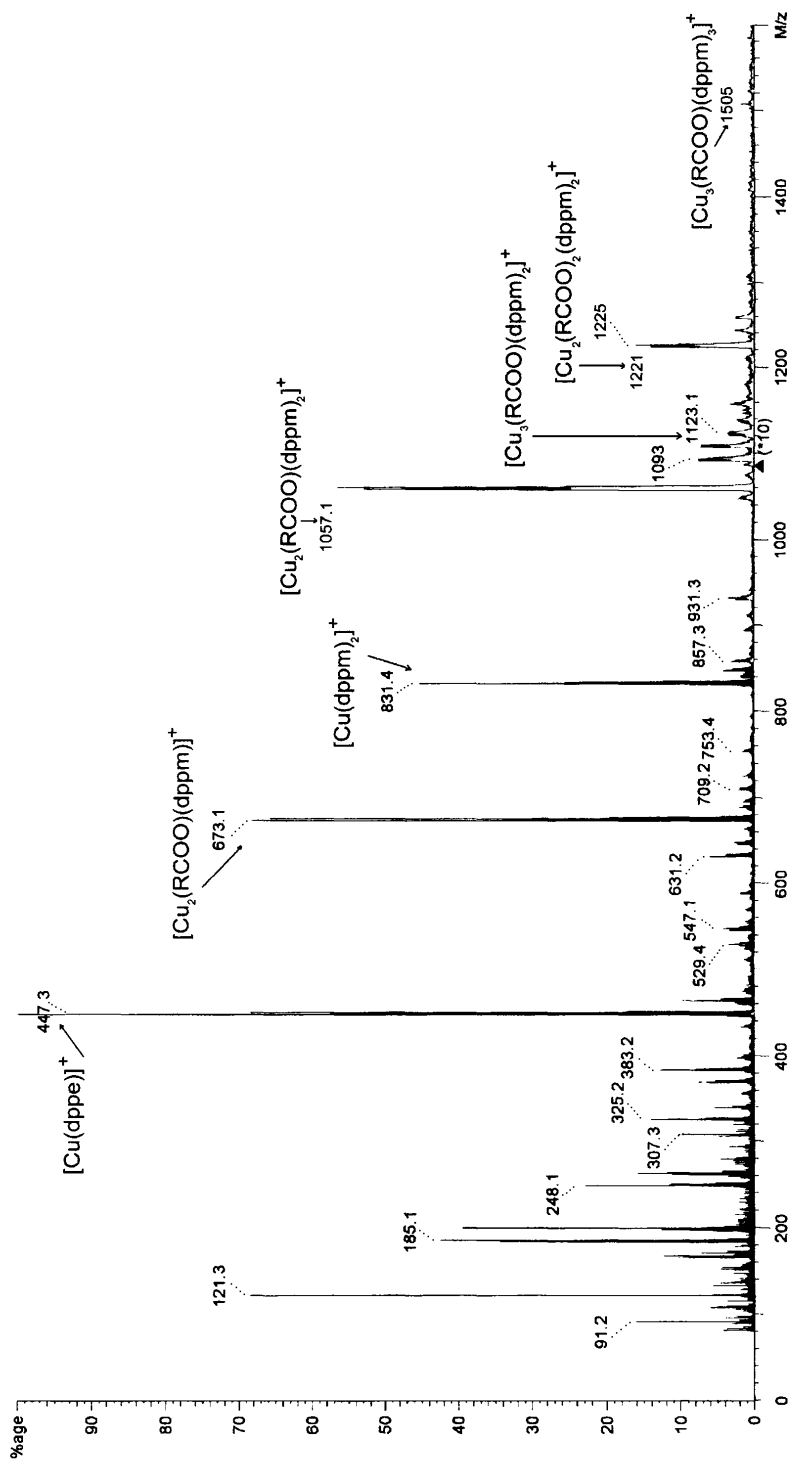
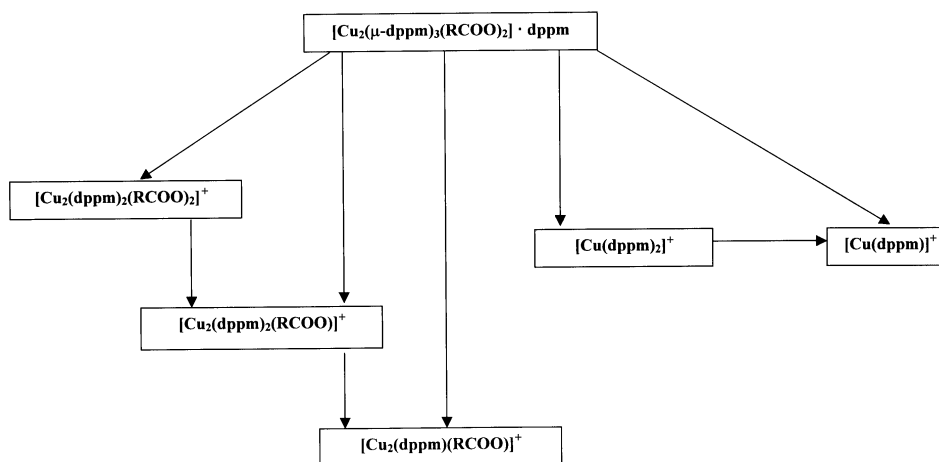


Figure 1. Mass spectrum of **1**  $[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_2\text{F}_5\text{COO})_2]\cdot\text{dppm}$ .



**Figure 2.** Fragmentation scheme for  $[\text{Cu}_2(\mu\text{-dppm})_3(\text{RCOO})_2]\cdot\text{dppm}$ .

dppm. Complicated pattern of LSIMS spectra did not allow a complete assignment of fragments, which have been formed during the partition and degradation processes. Nevertheless the structurally significant peaks can be rationalized in the fragmentation  $[\text{Cu}_2(\mu\text{-dppm})_3(\text{RCOO})_2]\cdot\text{dppm}$  scheme (Figure 2). Postulated mechanisms are based on the detected  $[\text{Cu}_2(\text{RCOO})_2(\text{dppm})_2]^+$ ,  $[\text{Cu}_2(\text{RCOO})(\text{dppm})_2]^+$ ,  $[\text{Cu}_2(\text{RCOO})(\text{dppm})]^+$  and  $[\text{Cu}_2(\text{RCOO})_2(\text{dppm})]^+$  fragments, what confirms the presence of the dimeric species in the solid state.

**Table 1.** LSIMS mass spectra of compounds 1–5 in the presence of NBA as liquid matrix (% relative abundance).

Detected species	1	2	3	4	5
$\text{Cu}_3(\text{RCOO})(\text{dppm})_3$	1505 (1%)	1605 (1%)	1705 (1%)	1806 (1%)	1856 (1%)
$\text{Cu}_2(\text{RCOO})_2(\text{dppm})_2$	1221 (16%)	–	–	–	–
$\text{Cu}_3(\text{RCOO})(\text{dppm})_2$	1123 (4%)	–	–	–	–
$\text{Cu}_2(\text{RCOO})(\text{dppm})_2$	1057 (52%)	1157 (50%)	1258 (45%)	1359 (50%)	1409 (54%)
$\text{Cu}(\text{dppm})_2$	831 (45%)	831 (45%)	831 (35%)	831 (25%)	831 (28%)
$\text{Cu}_2(\text{RCOO})(\text{dppm})$	673 (68%)	773 (100%)	873 (100%)	973 (100%)	1023 (78%)
$\text{Cu}(\text{dppm})$	447 (100%)	447 (100%)	447 (100%)	447 (100%)	447 (100%)

**NMR spectra analysis:** NMR spectroscopic analyses are indispensable and useful to elucidate the solution structure of the complexes.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  results of NMR solution spectra analysis are listed in Table 2.  $^1\text{H}$  NMR spectra of the complexes revealed broad multiplets centered at 3.1 ppm from the methylene protons in coordinated dppm. They are coupled with phosphorus, but we were unable to calculate the coupling constants from the spectra available. The chemical shift of the bridging methylene protons can be used for the evaluation of the charge changes on the coordi-

nating phosphorus atom. Using the equation, derived by Grim and Walton [10],  $\delta_{\text{CH}_2}(\text{ppm}) = 1.57\Sigma q_i + 2.65$ , where  $q_i$ -charge generated on each phosphorus atom, we have calculated the charge about +0.29 for the complexes and +0.10 for free dppm. The magnitude and direction of charge transfer from copper to phosphorus atoms 0.19 is in good correlation with Pauling's electronegativity of phosphorus (2.1) and copper (1.9) and  $\sigma$ -donation from phosphorus to the central ion.  $^{13}\text{C}$  resonances of COO group were observed as weak signals (161.6–162.0 ppm) shifted downfield in comparison to free acids (Table 2). In the case of **1**, **2**, **4** and **5** they were detected as triplets, due to the spin-spin coupling [ $^2J(^{13}\text{C}-^{19}\text{F}) = 23.9\text{--}24.8\text{ Hz}$ ]. The chemical shifts of carboxylic carbon are very similar within the series studied, indicating that their coordination modes may be related. The magnitude of COO coordination shifts defined as  $\Delta\delta = \delta_{\text{complex}} - \delta_{\text{free ligand}}$ ; ( $\Delta\delta_{\text{COO}} = 2.1\text{--}3.2\text{ ppm}$ ) is more pronounced for the complexes under discussion than for analogous compounds with 1,2-bis(diphenylphosphine)ethane (0.6–2.9). Observed COO coordination shift for analogous Cu(I) complexes with  $\text{P}(\text{OR})_3$  [11] is small, however, the coordination mode of carboxylates should be similar for both phosphines complexes. The small coordination shift is in favour of a weakly bonded carboxylate group in the series studied [12].

**Table 2.**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR chemical shifts [ppm].

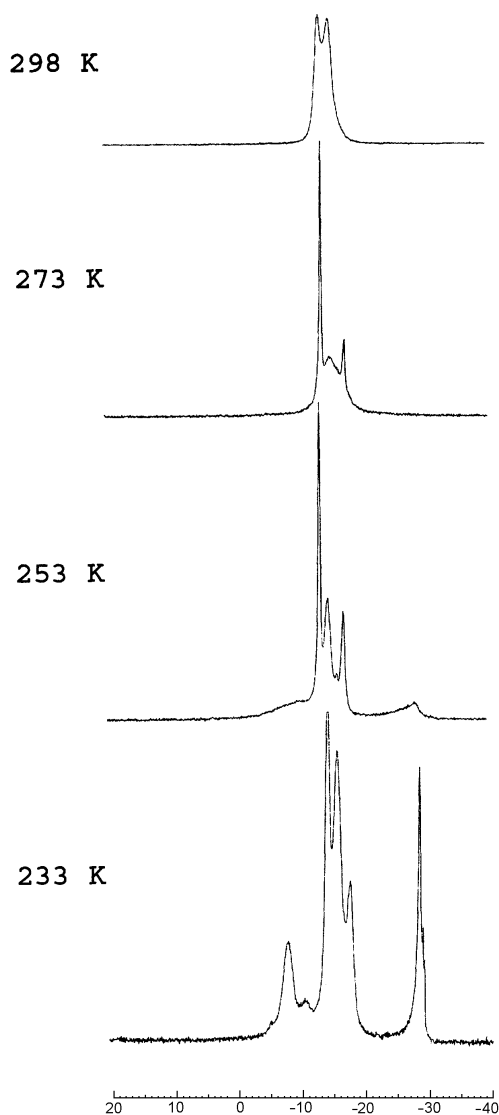
Complex	$\delta^1\text{H}$	$\delta_{\text{COO}}$	$\Delta\delta_{\text{COO}}$	$\delta_{\text{CF}_{2\alpha}}$	$\Delta\delta_{\text{F}\alpha}$	$\delta^{31}\text{P}$	$\Delta\delta_{\text{P}}$	$W_{1/2}$ (Hz)
$[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_2\text{F}_5\text{COO})_2]\cdot\text{dppm}$	3.12	162.0(t)	3.2	-41.4(s)	4.2	-14.2	7.5	243
$[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_4\text{F}_9\text{COO})_2]\cdot\text{dppm}$	3.12	161.6(t)	2.1	-38.2(t)	3.8	-13.8, -15.3	7.9, 6.4	263
$[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_6\text{F}_{13}\text{COO})_2]\cdot\text{dppm}$	3.11	161.7(s)	2.7	-38.1(s)	3.9	-14.5	7.2	243
$[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_8\text{F}_{17}\text{COO})_2]\cdot\text{dppm}$	3.11	161.6(s)	2.8	-37.9(s)	4.1	-14.4	7.3	206
$[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_9\text{F}_{19}\text{COO})_2]\cdot\text{dppm}$	3.11	161.7(t)	2.9	-37.8(s)	4.2	-14.3	7.4	243

s – singlet; t – triplet

$\Delta\delta_{\text{F}\alpha} = \delta_{\text{complex}} - \delta_{\text{acid}}$ ;  $\Delta\delta_{\text{COO}} = \delta_{\text{complex}} - \delta_{\text{acid}}$ ;  $\Delta\delta_{\text{P}} = \delta_{\text{complex}} - \delta_{\text{phosphine}}$ .

In  $^{19}\text{F}$  NMR spectra the most distinct changes were observed for  $\text{C}_\alpha\text{F}_2$  signals, which are shifted downfield  $\Delta\delta_{\text{F}\alpha} = 3.8\text{--}4.2\text{ ppm}$  in relation to free carboxylic acids (Table 2). Analogous effects were found in  $^{19}\text{F}$  NMR spectra of Cu(I), Ag(I), Au(I) complexes with perfluorinated carboxylates and tertiary phosphines [11,13–15]. The coordination shift of  $\text{C}_\alpha\text{F}_2$  can be rationalized as an additional evidence of the carboxylate complexation in solution. Coordination shift of  $\text{C}_\alpha\text{F}_2$ , detected in the spectra of the complexes, is similar to observed for analogous compounds with tertiary phosphites [11]. This can be related to carboxylate complexation, although it is difficult to correlate this effect with the mode of carboxylates binding.  $^{31}\text{P}$  NMR spectrum of complex **1** exhibits one line centered at 14.2 ppm, but in the case of **2** pseudo doublet at -13.8 and -15.3 ppm was observed (Figure 3). Spectrum of **2** obtained in temperature range 298–233 K revealed three groups of signals, which can be assigned to at least three different species, existing in equilibria (Figure 3). The fourth molecule of dppm is not

bonded directly to copper, hence it should be detectable in solution, however, the signal of free dppm was not observed in  $^{31}\text{P}$  NMR temperature variable spectra. This fact suggests a fast exchange of dppm with Cu(I) and participation of all dppm molecules in exchange processes with Cu(I). The  $^{31}\text{P}$  lines broadening in temperature-variable spectra suggest an unresolved  $^{31}\text{P}$ - $^1\text{H}$  coupling (Table 2). Besides the spectra of compounds **1–5** at 233 K revealed the broad singlets between  $-7.6 \div -8.2$  ppm. In the reported  $^{31}\text{P}$  NMR spectrum [16] of  $[\text{Cu}(\text{dppm})_2]\text{PF}_6$ , phosphorus signal was found at  $-6$  ppm, which with temperature decrease (to 175 K) has shifted to  $-8$  ppm without



**Figure 3.** Temperature variable  $^{31}\text{P}$  NMR spectra of **2**  $[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_4\text{F}_9\text{COO})_2]\cdot\text{dppm}$ .

splitting from  $^{63}\text{Cu}$  spin-spin coupling. Therefore, detected singlets are in favour of the  $[\text{Cu}(\text{dppm})_2]^+$  species present in solution. Observed signals pattern and coordination shifts allow the conclusion that  $\text{Cu}(\text{P})_4^+$  should exist as the most favorable coordination form in solution. For this system we have tried to register  $^{63}\text{Cu}$  NMR but the signals were not detectable, what can be caused by the fast quadrupole relaxation of  $^{63}\text{Cu}$  [16–18]. Signals observed in CPMAS  $^{31}\text{P}$  NMR are broad ( $\delta = -5$  ppm and  $w_{1/2} = 3000$  Hz). Observed broadening can be referred to the unresolved coupling to the copper nuclei and quadrupole interactions, what has been reported for other Cu(I) complexes with diphosphines [19].  $^{13}\text{C}$  CPTOSSB NMR spectra revealed two groups of signals: one between 129–142 ppm are assigned to phenyl carbons, whereas the second one, as a weak triplet centered at 33.7 ppm, to  $-\text{CH}_2-$  resonances. Their coordination shifts are small and not informative about complexes geometry.

**Infrared spectra analysis:** Carboxylate ions can coordinate to metal ions in a number of ways, such as monodentate, chelating or bridging [20–22], what can be concluded from the IR spectra analyses. Reported correlations between the mode of carboxylate linkage and COO group stretching frequencies prompted us to choose parameter  $\Delta_{\text{COO}} = \nu_{\text{as}} - \nu_{\text{s}}$  (as – asymmetric, s – symmetric) as an indicative parameter of coordination. Calculated  $\Delta_{\text{COO}}$  parameter was compared with the one obtained for sodium salts (Table 3). The value of  $\Delta_{\text{COO}}$  for the complexes under discussion is bigger than for sodium salts, but not as high as it was observed in the case of monodentately coordinated carboxylates (above  $310\text{ cm}^{-1}$ ) [9,21]. Therefore, we propose for carboxylate the monodentate bonding to Cu(I) ions. The monodentate coordination of COO was reported frequently for copper(I) compounds [8,9,23,24]. Spectra in the range of metal–ligand vibrations revealed bands, which could be assigned to Cu–O and Cu–P stretching vibrations. Assuming  $\text{C}_{3v}$  sphere geometry for complexes under discussion, one can expect in the spectrum bands from stretching vibrations of Cu–O of the type  $\text{A}_1$ , whereas from Cu–P stretching vibrations of the type  $\text{A}_2$  and E (all IR active). In the analysed spectra, bands in the range  $261\text{--}281\text{ cm}^{-1}$  can be assigned to Cu–O stretching vibrations. The absorption bands at  $160\text{--}164\text{ cm}^{-1}$  can be referred to the type E vibrations of Cu–P, whereas these between  $134\text{--}140\text{ cm}^{-1}$  to the type  $\text{A}_2$  [25] (Table 3). The complexes studied most probably appear to be dimers with a coordination sphere composed of bridging diphosphines between two copper ions and monodentately bonded carboxylates.

**Table 3.** Selected IR absorption bands ( $\text{cm}^{-1}$ ).

Compound	$\text{COO}_a$	$\text{COO}_s$	$\Delta\nu$	$\Delta\nu_1$	$\nu_a\text{Cu-P}$	$\nu_s\text{Cu-P}$	$\nu_s\text{Cu-O}$
$[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_2\text{F}_5\text{COO})_2]\cdot\text{dppm}$	1688	1395	293	268	160	135	224
$[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_4\text{F}_9\text{COO})_2]\cdot\text{dppm}$	1687	1397	290	270	160	138	230
$[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_6\text{F}_{13}\text{COO})_2]\cdot\text{dppm}$	1688	1397	291	272	164	140	226
$[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_8\text{F}_{17}\text{COO})_2]\cdot\text{dppm}$	1688	1398	290	272	160	136	225
$[\text{Cu}_2(\mu\text{-dppm})_3(\text{C}_9\text{F}_{19}\text{COO})_2]\cdot\text{dppm}$	1688	1399	289	276	164	138	230

$\Delta\nu = \nu_{a\text{COO}} - \nu_{s\text{COO}}$  for complexes;  $\Delta\nu_1 = \nu_{a\text{COO}} - \nu_{s\text{COO}}$  for sodium carboxylates.

## CONCLUSIONS

The new series of Cu(I) complexes with perfluorinated carboxylates and bis(diphenylphosphine)methane are in good correlation between the chemical shifts of methylene protons in the dppm and positive charge on the phosphorous atoms, which indicate a significant level of  $\sigma$ -bond between copper(I) and dppm. The complexes appear in dimeric forms, linked *via* bridges formed by dppm, what can be postulated from MS, IR and NMR spectra analyses. They appear most probably in tetrahedral coordination both in solution and in the solid state. The fast exchange in Cu(I) coordination sphere resulted in the lack of signals from  $^{63}\text{Cu}$  NMR, but three signals in  $^{31}\text{P}$  NMR were detected. The most favorable coordination geometry in solution appears to be  $\text{Cu}(\text{P})_4^+$ , which is in a fast exchange with other species.

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