New Polymeric Copper(II) Complexes with Tributyl Phosphite and Perfluorinated Carboxylates

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(d A 21 , 2000; d u ob 2d , 2000)

New Cu(II) complexes with tributyl phosphite and aliphatic perfluorinated carboxylates $[Cu\{P(OBu)_3\}(\mu\text{-}OH)(\mu\text{-}RCOO)]_n$, where R = CF_3, C_2F_5, C_3F_7, C_6F_{13}, C_7F_{15}, were obtained and their spectroscopic (UV-VIS, EPR, MS, IR) and thermal properties were studied. Mass spectra were in favour of the bridging coordination carboxylates and monodentate phosphite and suggest a polymeric structure. EPR spectra and magnetic susceptibility measurements indicate the formation of pentacoordinated Cu(II) in polymeric complexes. Ew-32

with carboxylates originate usually as dimers with carboxylate bridges and organic ligands in axial positions. Because the perfluorinated carboxylates are weaker -donors than nonfluorinated analogues, hence one can expect a different way of coordination. In the presence of -acceptor such as $P(OBu)_3$, Cu(II) complexes should be less stable, what may result in multinuclear species of Cu(II). In this paper we describe the synthesis and spectroscopic studies of new Cu(II) complexes $[Cu\{P(OBu)_3\}(\mu\text{-}OH)(\mu\text{-}RCOO)]_n$, where R = CF_3, C_2F_5, C_3F_7, C_6F_{13}, C_7F_{15}. Thermal decomposition process was examined with the aim to determine the suitability of complexes as precursors for Chemical Vapour Deposition (CVD), because Au(I), Ag(I) and Cu(I) complexes with perfluorinated carboxylates and phosphines or phosphites revealed sufficient volatility for CVD [9–14].

EXPERIMENTAL

Chemicals: Tributyl phosphite (96%) and perfluorinated carboxylic acids (97–99%) were purchased from Aldrich and used without purification. Acetonitrile (Aldrich hplc grade) was dried over molecular sieves 4 Å, next over CaH_2 and distilled under dry nitrogen from P_4O_{10} prior to use. Copper powder for organic synthesis (Aldrich) and $CuCO_3$ nH_2O analytical grade from POCh (Poland) were used as received.

Instrumentation: IR spectra were performed with a Perkin–Elmer 2000 FT IR spectrophotometer in the range 4000–400 cm^{-1} using film on KBr plates at room temperature and at 78 K, whereas 400–100 cm^{-1} spectra were recorded using film on polyethylene plates. Thermal studies were performed with an OD-102 Derivatograph MOM (Hungary), in nitrogen or air; the heating range: 293–773 K, heating rate 2.5 /min, sample mass 50 mg and TG range 50 mg; the reference material was Al_2O_3. Powder diffractograms were recorded on an HZ64/A-2 DRON-1 diffractometer using CuK radiation. Absorption UV-VIS (200–833 nm) spectra in the solid state were measured with a M40 Carl Zeiss Jena spectrophotometer. EPR spectra were recorded with an ESR Bruker Physik B-ER-418 S reflection type spectrometer in X-band at room temperature. The magnetic field was measured with an automatic NMR-type magnetometer. The microwave frequency was monitored with a Hewlett-Packard frequency divider. Magnetic susceptibility was measured in the range 80–300 K by the Faraday method with $Hg[Co(NCS)_4]$ as a calibrant. Copper determination was made by AAS method with an AAS PU 9100 X Philips spectrophotometer but C and H by semi-microanalysis. Mass spectra were registered with an AMD-640 spectrometer, using electron ionization method, in temperature range 295–573 K.

Synthesis: Direct reaction of tributyl phosphite with Cu(II) carboxylates results in the reduction of Cu(II) and formation of Cu(I) species and tributyl phosphite oxide [1,2]. Therefore, Cu(I) complexes $[Cu_2\{P(OBu)_3\}_2(\mu\text{-}RCOO)_2]$ were used as substrates for the synthesis of Cu(II) compounds. In the general procedure, copper(II) carboxylate (0.5 10^{-3} moles), of the above formula, was placed in the Schlenk tube (in argon atmosphere), dissolved or suspended in 20 cm^3 of freshly distilled acetonitrile and copper powder (2.5 10^{-3} moles) was added. Obtained suspension was stirred until the solution became pale yellow. Next $P(OBu)_3$ (1.0 10^{-3} moles) was added, reaction mixture stirred for about 12 h at ambient temperature, filtered and the solvent evaporated on vacuum line, leaving the pale yellow viscous liquids [14]. Acetonitrile solutions of the mentioned complexes were oxidized by air during 10 minutes. The resulting green solutions were left in nitrogen until solids with a constant stoichiometry were formed. We were unable to obtain crystals suitable for X-ray analysis, because the complexes decomposed in the following solvents: benzene, toluene, alcohols, ethers and chlorinated hydrocarbons . The differences between

RESULTS AND DISCUSSION

Mass Spectrometry : In order to confirm the stoichiometry and fragmentation mechanism the EI spectra were recorded. Due to the natural abundance of ^{63}Cu (69.1%) and ^{65}Cu (31.9%) isotopes in compounds, which have one copper atom, two signals with 2:1 intensity should be observed. Species with two copper atoms should reveal three peaks with the characteristic 4:4:1 intensity pattern, but the multinuclear fragments should disclose even more complicated patterns. In the EI mass spectra the following fragments: $[Cu_2(RCOO)\{P(OBu)_3\}]^+$, $[Cu_2(RCOO)_2]^+$, $[Cu_2(RCOO)]^+$ and $[Cu\{P(OBu)_3\}]^+$ were detected respectively at: (**1**) 489, 352, 239, 313; (**2**) 539, 452, 289; (**3**) 589, 552, 339, 313; (**4**) 739, 852, 489, 313 [m/e]. These results are in favour of the bridging carboxylates and monodentate phosphite. Signals with intensity < 0.5%, characteristic for multinuclear fragments (with three, four . copper atoms), were also detected, what suggests the polymeric structure. This mass spectrometry identification of copper containing fragments is consistent with the spectroscopic results (*d*).

I R Spectra analysis: Examination of the infrared spectra (4000–100 cm^{-1}) was performed to determine the ligands binding and the symmetry of the coordination sphere. Coordination mode of the carboxylic acids residues can be proposed from the analysis of the COO asymmetrical ($_{as}$) and symmetrical ($_{s}$) stretching vibration frequencies. Absorption bands of COO vibrations were detected respectively in the range 1689–1694 cm^{-1}. The band of $_{s}$COO vibration and the one at 1383 cm^{-1} for tributyl phosphite coincide at room temperature. Therefore, we have assigned the frequency of $_{s}$COO from low-temperature spectra in the range 1403–1434 cm^{-1} (Table 1). As a criterion of carboxylates binding mode we have applied the parameter $_{COO}$ = $_{as}$ – $_{s}$ [15–16]. The estimation of the carboxylate linkage with the metal ion is based on the relation between $_{COO}$, calculated for the complex considered and $_{COO}$ found in the identical sodium carboxylate and analogues Cu(II) complexes with $P(OMe)_3$ and $P(OPh)_3$ [6,7]. The magnitudes of calculated $_{COO}$ for the complexes are in favour of the bridging coordination (Table 1). This fact has confirmed the results of the mass spectra analysis and has further evidences in EPR and magnetic measurements (*d*).

Table 1. IR spectral frequencies [cm^{-1}].

Complex	$_{as}$(COO)	$_{s}$(COO)	$_{COO}$	$_{1}$	$_{as}$(P–O)	$_{s}$(CuO)	(CuP)	(OH)
1) $[Cu\{P(OBu)_3\}(\ \text{-OH})(\ \text{-}CF_3COO)]_n$	1689	1434	255	223	824	219	157	3420
2) $[Cu\{P(OBu)_3\}(\ \text{-OH})(\ \text{-}C_2F_5COO)]_n$	1693	1411	282	268	820	224	150	3344
3) $[Cu\{P(OBu)_3\}(\ \text{-OH})(\ \text{-}C_3F_7COO)]_n$	1694	1407	287	272	814	225	157	3464
4) $[Cu\{P(OBu)_3\}(\ \text{-OH})(\ \text{-}C_6F_{13}COO)]_n$	1694	1403	291	272	810	224	152	3378
5) $[Cu\{P(OBu)_3\}(\ \text{-OH})(\ \text{-}C_7F_{15}COO)]_n$	1694	1403	291	272	811	234	153	3380

$_{COO}$ = $_{as}$(COO) – $_{s}$(COO) for complex, $_{1}$ = $_{as}$(COO) – $_{s}$(COO) for RCOONa, $_{as}$(P–O) = 775 cm^{-1} for free $P(OBu)_3$.

The absorption band from P–O stretching vibrations $_{as}$(P–O) is the most sensitive on coordination of P(OBu)$_3$. In Cu(I) complexes with coordinated phosphites this band was shifted towards higher wavenumbers . 20–50 cm^{-1} [17,18]. In the spectra of the compounds discussed $_{as}$(P–O) was detected between 810–824 cm^{-1} (Table 1), . . 35–49 cm^{-1} higher than for free tbp [19], what is an additional evidence of tributyl phosphite metallation. We did not observe the band characteristic for tributyl phosphite oxide (P=O) at 1274 cm^{-1}, what excludes the oxidation of the phosphorous ligand and is in favour of the copper(II)–phosphorus(III) bond [20]. The strong absorption band in the range 3344–3464 cm^{-1} can be assigned to the stretching vibrations of the bridging OH (Table 1) [16]. Moreover, the broad and strong band from the intermolecular hydrogen bonds between OH and fluorine atoms has been found between 3200 and 3500 cm^{-1}. Spectra in the range of metal–ligand vibrations revealed bands, which can be assigned to Cu–O(OOCR) and Cu–P stretching vibrations. Stretching vibrations of Cu–O(OOCR) bonds from group theory calculations (for C_2 symmetry) should be of the type A_1 and B_1 (IR active). Therefore, for $_s$(CuO) vibrations we have assigned bands in the range 219–234 cm^{-1} (A_1), what agrees well with the data reported [21]. The bands of $_{as}$(CuO) and (Cu–OH) stretching vibrations coincide with the strong tbp bands (observed at 381 and 289 cm^{-1}

with different coordination numbers, but we can exclude the geometry of the flattened tetrahedron [25].

Magnetic measurements: The molar susceptibilities were corrected for the diamagnetism, using Pascal's constants and the temperature independent paramagnetism equals: ${}_{K} = 60\ 10^{-6}$ cm^3/mol for copper(II) ion. The effective magnetic moments were calculated as: $\mu_{eff} = 2.828[({}^{M}_{corr} + {}_{K})T]^{1/2}$ and their values were in the range 1.46–1.60 μ_B at room temperature. The temperature dependencies of magnetic susceptibilities obey the Curie-Weiss law, . . ${}^{M}_{corr} = C/(T - \ )$, where $C = Ng^2\ {}^{2}_{B} S(S + 1)/3k$ with $S = 1/2$. The best fit values of the Curie (C) and Weiss constants ( ) are listed in Table 2. Weiss constant is negative (from –76 K for **1** to –50 K for lapping processes of ligands decomposition and dissociation have been observed for $[Cu\{P(OR\ )_3\}(\mu\text{-}OH)(\mu\text{-}RCOO)]_n$, R = Me, Ph [6,7]. The complexity of the decomposition resulted also in a different sample weight loss in the first stage. Compound **1** lost 44%, whereas **2** and **3** much lower (3.1 and 11%), when **4** and **5** lost 78 and 77% respectively (Table 3). Such diversity can be related to the different samples crystalline forms, elementary cell parameters and/or variation in Cu–O(RCOO) distances. Examined lines on powder diffractograms of the final product were as follows: Cu_2O – 0.249, 0.215, 0.175, 0.151 nm; $Cu_2P_2O_7$ – 0.314, 0.295, 0.292, 0.253 nm and correspond to the reported in Powder Diffraction File [27]. Analysis of TG curves and powder diffractograms proved, that majority of complexes decomposes to a mixture of Cu_2O and $Cu_2P_2O_7$ (1:1 ratio), however, for the complex **2** excess of copper(II) diphosphate was observed, whereas for **4** it was the only product.

Table 3. Results of thermal analysis in nitrogen.

Complex	Heat effect	Temperature [K]			Weight loss on TG [%]		Final product
		T_i	T_m	T_f	found	calc.	$xCu_2O:yCu_2P_2O_7$
1) $[Cu\{P(OBu)_3\}(\ \text{-}OH)(\ \text{-}CF_3COO)]_n$	exo/endo	363	483	498$^{a)}$	44.0		
	endo	498$^{a)}$	518	548	31.0	75.0	1:1
2) $[Cu\{P(OBu)_3\}(\ \text{-}OH)(\ \text{-}C_2F_5COO)]_n$	exo	318	378	408	3.1		
	exo	408	488, 538	608	72.9	75.9	2:3
3) $[Cu\{P(OBu)_3\}(\ \text{-}OH)(\ \text{-}C_3F_7COO)]_n$	exo	343	513	543	11.0		
	exo	543	623	658	69.0	79.6	1:1
4) $[Cu\{P(OBu)_3\}(\ \text{-}OH)(\ \text{-}C_6F_{13}COO)]_n$	endo	368	503	528	78.0	78.3	0:1
5) $[Cu\{P(OBu)_3\}(\ \text{-}OH)(\ \text{-}C_7F_{15}COO)]_n$	exo	318	528	573	77.0		
	exo	573	613	713	8.0	85.0	1:1

T_i – initial temperature, T_m – maximum temperature, $T_{\text{– initial T}}$

Table 4. Results of thermal analysis in air.

Complex	Heat effect	Temperature [K]			Weight loss on TG [%]		Final product
		T_i	T_m	T_f	found	calc.	$xCu_2O:yCu_2P_2O_7$
1) $[Cu\{P(OBu)_3\}($ -OH)(-CF_3							

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