



# Studies of new volatile copper(I) complexes with triphenylphosphite and perfluorinated carboxylates

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Received 9 March 1999; accepted 9 July 1999

## Abstract

Copper(I) complexes with triphenylphosphite and aliphatic perfluorinated carboxylates of the type  $[\text{Cu}(\mu\text{-RCOO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}]_2$ , where  $\text{R}=\text{CF}_3$ ,  $\text{C}_2\text{F}_5$ ,  $\text{C}_3\text{F}_7$ ,  $\text{C}_6\text{F}_{13}$ ,  $\text{C}_7\text{F}_{15}$ ,  $\text{C}_8\text{F}_{17}$  and  $\text{C}_9\text{F}_{19}$  have been prepared as viscous liquids and characterised by  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ,  $^{63}\text{Cu}$  NMR, IR and mass spectra. In the liquid state, a dimeric structure with Cu in trigonal symmetry linked by the bridging carboxylates is proposed. Temperature-dependent  $^{31}\text{P}$  and  $^{63}\text{Cu}$  NMR spectra were determined, in the 333–233 K range and single lines from both nuclei were detected, suggesting the fast exchange of triphenylphosphite in acetonitrile solution. Copper relaxation is sufficiently slow to record the signal, which is the first time that this has been reported for complexes with  $\text{P}(\text{OC}_6\text{H}_5)_3$ . Examination of  $^{13}\text{C}$  and  $^{19}\text{F}$  resonances confirm coordination of carboxylates in solution where few dimeric species with a geometry lower than  $T_d$  symmetry can exist. Thermal decomposition of complexes proceeds as a multistage process, yielding a mixture of Cu,  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{P}_2\text{O}_7$ . © 1999 Elsevier Science Ltd. All rights reserved.

**Keywords:** Copper(I); Triphenylphosphite; NMR spectra

## 1. Introduction

Copper(I) complexes with oxygen donor ligands such as carboxylates have mono- or multinuclear structures depending on the nature of the carboxylate and other ligands in the coordination sphere [1–4]. These compounds have been studied less than Cu(II) analogues due to the instability of copper(I)–oxygen bonds. One can explain this as a weak bond between hard oxygen and soft Cu(I) using the theory of hard–soft acids–bases [5]. Our interest was focused on perfluorinated carboxylates in which oxygen atoms could perform as a harder donor, rather than in the nonfluorinated analogues, hence, one may expect that they could be bonded in Cu(I) complexes in different ways that may result in interesting new structures. Tertiary phosphines, as  $\pi$ -electroacceptor ligands, are likely to stabilise Cu(I) complexes, which may also have effects upon the strength of the Cu–O bond. Therefore, we have chosen triphenylphosphite  $[\text{P}(\text{OC}_6\text{H}_5)_3]$ , tpp, as the ligand, as it should exhibit stronger  $\pi$ -acceptor properties than tri-

phenylphosphine and smaller steric hindrances because phenyl rings are more flexible along the C–O–P bond [6]. We assumed that these features would be effective in complex stabilisation and in the preparation of Cu(I) complexes. The main purpose of the presented work was isolation of new Cu(I) complexes and to elucidate the coordination sphere composition and symmetry using  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$ ,  $^{63}\text{Cu}$  NMR, mass spectra and infrared results. Due to fast ligand exchange at the labile Cu(I) centre,  $^{31}\text{P}$  and  $^{63}\text{Cu}$  NMR studies have been used relatively infrequently for determining the structural characteristics of copper(I) complexes. Besides the good NMR sensitivities of  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , the significant quadrupole moments imply that only a limited number of copper resonances have been observed in solution [7–10] and, in this paper, we report on further examples. We have found that gold(I) and silver(I) complexes with perfluorinated carboxylates and tertiary phosphines presented sufficient volatility for chemical vapour deposition (CVD) [11–15], hence, the other purpose of this work was to prepare volatile precursors for CVD of copper oxide or copper metal thin films. Thermal studies were undertaken to determine the mechanism of thermal decomposition and to ascertain the

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suitability of complexes as precursors for CVD, which should be competitive to organometallics used at present.

## 2. Experimental

### 2.1. Materials

Triphenylphosphite (99%) and perfluorinated carboxylic acids (97–99%) were purchased from Aldrich and were used without further purification. Acetonitrile, of analytical grade (Fluka), was dried over molecular sieves 4A, then over  $\text{CaH}_2$  and, finally, was distilled under dry nitrogen from  $\text{P}_4\text{O}_{10}$  prior to use. Copper powder for organic synthesis (Aldrich) and copper(II) basic carbonate (analytical grade) from POCh (Poland) were used as received. Sodium carboxylates, for NMR and IR experiments, were obtained from sodium bicarbonate (POCh) and perfluorinated carboxylic acids from the same batch as above.

### 2.2. Methods

NMR spectra in acetonitrile were recorded using a Varian Gem. 200 MHz spectrometer;  $^{13}\text{C}$  was recorded at a frequency 50 MHz and using TMS as the standard,  $^{19}\text{F}$  was recorded at 188 MHz, with  $\text{CFCl}_3$  as a standard,  $^{31}\text{P}$  was recorded at 80.95 MHz and the standard used was 80%  $\text{H}_3\text{PO}_4$ ,  $^{63}\text{Cu}$  was recorded at 56.79 MHz with  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  as the standard. Temperature-dependent  $^{31}\text{P}$  and  $^{63}\text{Cu}$  NMR spectra (333–223 K) were obtained using a Bruker MSL 300 MHz spectrometer in the same solvent and using the same standards. To measure the linewidth of the peaks accurately, no baseline correction or apodization function was used in the data processing. Linewidths were measured using manual optimisation within the peakfinder module. The error in linewidth measurements was assumed to be equal to the digital resolution, which was 1.95 Hz. IR spectra were determined using a Perkin-Elmer 2000 FT IR spectrophotometer in the range 4000–400  $\text{cm}^{-1}$  using film on KBr plates, whereas 400–100  $\text{cm}^{-1}$  spectra were run using film on polyethylene plates. Thermal studies were performed on a MOM OD-102 Derivatograph (Paulik and Paulik, Hungary). The atmosphere over the sample was nitrogen, the heating range was 20–500°C, at a heating rate of 2.5 °/min, the sample mass was 20–90 mg, the TG range was 50 or 100 mg and the reference material was  $\text{Al}_2\text{O}_3$ . Powder diffractograms were recorded on an HZ64/A-2 DRON-1 (Russian Federation) diffractometer using  $\text{CuK}_\alpha$  radiation, with  $\lambda=0.1542$  nm. Copper was determined using a Carl Zeiss Jena AAS spectrometer with  $\text{Cu}(\text{NO}_3)_2$  solution as the standard. Mass spectra were recorded on an AMD-640 mass spectrometer using the electron ionization method.

### 2.3. Synthesis

Copper(II) carboxylates of the general formula  $\text{Cu}(\text{RCOO})_2$  where  $\text{R}=\text{CF}_3$ ,  $\text{C}_2\text{F}_5$ ,  $\text{C}_3\text{F}_7$ ,  $\text{C}_6\text{F}_{13}$ ,  $\text{C}_7\text{F}_{15}$ ,  $\text{C}_8\text{F}_{17}$  and  $\text{C}_9\text{F}_{19}$  were prepared by reaction of a slight excess of copper(II) basic carbonate with the respective carboxylic acid in a water or water–ethanol solution. The copper content, thermal analysis, mass and IR spectra confirmed the compositions of the carboxylates obtained.

Complexes of Cu(I) were synthesised in Schlenk glassware in an argon atmosphere. In the general procedure, copper(II) carboxylate ( $0.5 \times 10^{-3}$  mol) of the above formula was placed in the Schlenk tube, either dissolved or suspended in 20  $\text{cm}^3$  of freshly distilled acetonitrile, and copper powder ( $2.5 \times 10^{-3}$  mol) was added. The suspension obtained was stirred until the solution was pale yellow in colour. Next,  $\text{P}(\text{OC}_6\text{H}_5)_3$  ( $1.0 \times 10^{-3}$  mol) was added and the reaction mixture was stirred for about 12 h at ambient temperature, filtered and the solvent was evaporated in a vacuum line, leaving a pale yellow viscous liquid. The complexes were unstable in air, turning green. The results of Cu determination were as follows (%) (calc./found): (1)  $\text{C}_{40}\text{H}_{30}\text{Cu}_2\text{F}_6\text{O}_{10}\text{P}_2$ , Cu (13.0/12.9); (2)  $\text{C}_{42}\text{H}_{30}\text{Cu}_2\text{F}_{10}\text{O}_{10}\text{P}_2$ , Cu (11.8/11.6); (3)  $\text{C}_{44}\text{H}_{30}\text{Cu}_2\text{F}_{14}\text{O}_{10}\text{P}_2$ , Cu (10.8/10.8); (4)  $\text{C}_{50}\text{H}_{30}\text{Cu}_2\text{F}_{26}\text{O}_{10}\text{P}_2$ , Cu (8.6/8.2); (5)  $\text{C}_{52}\text{H}_{30}\text{Cu}_2\text{F}_{30}\text{O}_{10}\text{P}_2$ , Cu (8.1/7.9); (6)  $\text{C}_{54}\text{H}_{30}\text{Cu}_2\text{F}_{34}\text{O}_{10}\text{P}_2$ , Cu (7.6/7.3); (7)  $\text{C}_{56}\text{H}_{30}\text{Cu}_2\text{F}_{38}\text{O}_{10}\text{P}_2$ , Cu (7.2/7.0). The EI mass spectra were recorded for the complexes in an attempt to confirm the formulations. The fragments confirming stoichiometric composition were  $[\text{Cu}_2(\text{RCOO})_2\{\text{P}(\text{OC}_6\text{H}_5)_3\}]^+$  and  $[\text{Cu}_2(\text{RCOO})_2]^+$ . They were detected at (1) 662, 352; (2) 762, 452; (3) 862, 552; (4) 1162, 852; (5) 1262, 952; (6) 1362, 1052, respectively, whereas for (7), only  $[\text{Cu}_2(\text{RCOO})_2]^+$  at 1152 was found. The mass spectra results suggest a dimeric structure for the compounds and proved that the formulas proposed above were correct.

## 3. Results and discussion

### 3.1. IR spectral analysis

Mode of carboxylic acids residues coordination can be proposed from COO asymmetrical and symmetrical vibrations bands frequency analysis. Absorption bands of COO asymmetrical and symmetrical modes appeared in the ranges 1672–1690  $\text{cm}^{-1}$  and 1395–1432  $\text{cm}^{-1}$ , respectively (Table 1). As a spectroscopic criterion of carboxylates binding mode we have applied the parameter defined as  $\Delta\nu_{\text{COO}} = \nu_{\text{asym}} - \nu_{\text{sym}}$  [1,16–18]. Estimation of the carboxylate linkage with a metal ion is based on the relation between the  $\Delta\nu_{\text{COO}}$  value calculated for the considered complex and the  $\Delta\nu_{\text{COO}}$  value found in the

Table 1  
Characteristic IR spectral frequencies [ $\text{cm}^{-1}$ ]<sup>a</sup>

Compound	$\nu_a(\text{COO})$	$\nu_s(\text{COO})$	$\Delta$	$\Delta_1$	$\nu_a(\text{P-O})$	$\nu_a(\text{Cu-O})$	$\nu_s(\text{Cu-O})$	$\nu(\text{Cu-P})$
(1) $[\text{Cu}(\mu\text{-CF}_3\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}]_2$	1676	1432	244	223	890	273	210	160
(2) $[\text{Cu}(\mu\text{-C}_2\text{F}_5\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}]_2$	1690	1404	286	268	890	296	226	149
(3) $[\text{Cu}(\mu\text{-C}_3\text{F}_7\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}]_2$	1690	1395	295	272	885	293	218	149
(4) $[\text{Cu}(\mu\text{-C}_6\text{F}_{13}\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}]_2$	1691	1401	290	272	890	294	220	150
(5) $[\text{Cu}(\mu\text{-C}_7\text{F}_{15}\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}]_2$	1672	1404	268	272	890	293	206	148
(6) $[\text{Cu}(\mu\text{-C}_8\text{F}_{17}\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}]_2$	1694	1401	293	272	888	295	218	145
(7) $[\text{Cu}(\mu\text{-C}_9\text{F}_{19}\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}]_2$	1681	1410	271	276	895	292	206	152

<sup>a</sup>  $\Delta = \nu_a(\text{COO}) - \nu_s(\text{COO})$  for complex;  $\Delta_1 = \nu_a(\text{COO}) - \nu_s(\text{COO})$  for  $\text{RCOONa}$ ;  $\nu_a(\text{P-O}) = 863 \text{ cm}^{-1}$  for  $\text{P}(\text{OC}_6\text{H}_5)_3$ .

identical sodium carboxylate. The parameter  $\Delta\nu_{\text{COO}}$ , calculated for the examined complexes, was compared to  $\Delta\nu_{\text{COO}}$  for the appropriate sodium carboxylate and the data from mass spectra favoured a bridging coordination (Table 1).

Absorption bands of  $\nu(\text{P-O})$  in the examined spectra appeared in the region  $885\text{--}895 \text{ cm}^{-1}$  (Table 1), whereas in the spectrum of free tpp, they were at  $863 \text{ cm}^{-1}$  [19]. Such a significant change can be taken as evidence of triphenylphosphite coordination [20,21].

Spectra in the range of metal–ligand vibrations revealed bands that could be assigned to  $\text{Cu-O(RCOO)}$  and  $\text{Cu-P}$  stretching vibrations. From group theory calculations, for  $\text{C}_{2v}$  coordination sphere geometry, stretching vibrations of  $\text{Cu-O(RCOO)}$  should be of the type  $A_1$  and  $B_1$ , whereas  $\text{O-Cu-O}$  angle deformation modes should be of the type  $B_1$  and all of them were active in IR spectrum. The  $\text{Cu-O(RCOO)}$  stretching vibration bands were found in the range  $273\text{--}296 \text{ cm}^{-1}$  ( $B_1$ ) and  $200\text{--}226 \text{ cm}^{-1}$  ( $A_1$ ), corresponding to the data reported [2]. The absorption band observed in the range  $148\text{--}160 \text{ cm}^{-1}$  most likely can be assigned to  $\text{Cu-P}$  vibrations [22–24]. These results and fragments detected in mass spectra are in favour of a dinuclear structure of complexes with bridging carboxylates and a monodentate-coordinated molecule of triphenylphosphite.

### 3.2. NMR spectral analysis

The chemical shifts for  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  and  $^{63}\text{Cu}$  NMR resonances of the complexes are listed in Table 2.

Table 2  
 $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  and  $^{63}\text{Cu}$  NMR spectral data<sup>a</sup>

Compound	$^{13}\text{C}$ [ppm]				$^{19}\text{F}$ [ppm]				$^{31}\text{P}$ [ppm]		$^{63}\text{Cu}$	
	$\delta_{\text{C}}\text{COO}^-$	$\Delta_1$	$\delta_{\text{C}}\text{C}_\alpha\text{F}_2$	$\Delta_2$	$\Delta_3$	$\delta_{\text{C}}\text{CF}_3$	$\Delta_4$	$\Delta_5$	$\delta_{\text{C}}\text{P}$	$\Delta_6$	$\delta_{\text{C}}$ [ppm]	$\Delta\nu_{1/2}$ [Hz]
(1) $[\text{Cu}(\mu\text{-CF}_3\text{COO})\{\text{P}(\text{OPh})_3\}]_2$	159.0	0.6	—	—	—	3.2	1.9	0.4	109.8	−20.9	97.0	8750
(2) $[\text{Cu}(\mu\text{-C}_2\text{F}_5\text{COO})\{\text{P}(\text{OPh})_3\}]_2$	159.3	0.1	−41.4	4.2	0.7	−4.9	1.8	−0.2	108.2	−22.5	105.0	22520
(3) $[\text{Cu}(\mu\text{-C}_3\text{F}_7\text{COO})\{\text{P}(\text{OPh})_3\}]_2$	159.4	−0.2	−39.7	3.7	0.6	−4.0	0.6	−0.4	108.0	−22.7	64.2	11400
(4) $[\text{Cu}(\mu\text{-C}_6\text{F}_{13}\text{COO})\{\text{P}(\text{OPh})_3\}]_2$	159.0	−0.3	−37.2	4.8	1.7	−3.3	0.5	0.0	108.9	−21.8	110.0	9280
(5) $[\text{Cu}(\mu\text{-C}_7\text{F}_{15}\text{COO})\{\text{P}(\text{OPh})_3\}]_2$	159.0	−0.4	−37.7	4.2	1.2	−3.2	0.6	0.2	110.1	−20.6	125.0	13250
(6) $[\text{Cu}(\mu\text{-C}_8\text{F}_{17}\text{COO})\{\text{P}(\text{OPh})_3\}]_2$	159.1	−0.2	−37.8	4.0	1.0	−3.1	0.9	0.3	109.0	−21.7	105.0	8150
(7) $[\text{Cu}(\mu\text{-C}_9\text{F}_{19}\text{COO})\{\text{P}(\text{OPh})_3\}]_2$	159.3	−0.1	−38.0	3.9	<sup>b</sup>	−3.6	0.2	<sup>b</sup>	109.1	−21.6	150.0	20140

<sup>a</sup>  $\Delta_1 = \delta_{\text{C}}\text{COO}^- - \delta_{\text{C}}\text{COO}^-$ ;  $\Delta_2 = \delta_{\text{C}}\text{C}_\alpha\text{F}_2 - \delta_{\text{C}}\text{C}_\alpha\text{F}_2$ ;  $\Delta_3 = \delta_{\text{C}}\text{C}_\alpha\text{F}_2 - \delta_{\text{C}}\text{C}_\alpha\text{F}_2$ ;  $\Delta_4 = \delta_{\text{C}}\text{CF}_3 - \delta_{\text{C}}\text{CF}_3$ ;  $\Delta_5 = \delta_{\text{C}}\text{CF}_3 - \delta_{\text{C}}\text{CF}_3$ ;  $\Delta_6 = \delta_{\text{C}} - \delta_{\text{C}} \text{P}(\text{OC}_6\text{H}_5)_3$ ;  $\delta_{\text{C}} \text{P}(\text{OC}_6\text{H}_5)_3 = 130.7 \text{ ppm}$ ; C, complex; A, carboxylic acid; S, sodium carboxylate.

<sup>b</sup> Due to the low solubility of  $\text{C}_9\text{F}_{19}\text{COONa}$ , its spectrum could not be recorded.

One might expect that the  $^{13}\text{C}$  resonance of the  $\text{COO}$  carbon would give rise to the most significant changes upon coordination, but spectra of the complexes studied exhibit a very weak  $\text{COO}$  signal that was shifted slightly in relation to free acids (Table 2).

The fluorine resonances have been affected by  $\text{Cu-O}$  bond formation in a more pronounced way than carbon and the most distinct changes were observed for  $\text{C}_\alpha\text{F}_2$  signals (Table 2). The resonance lines of the  $\text{C}_\alpha\text{F}_2$  groups upon coordination were shifted downfield ( $\Delta_2 = 3.7\text{--}4.8 \text{ ppm}$ ) in relation to the spectra for free acids. The coordination shift observed for  $\text{C}_\alpha\text{F}_2$  can be taken as evidence of carboxylate complexation in acetonitrile solution. Analogous effects were observed in the spectra of  $\text{Ag(I)}$  and  $\text{Au(I)}$  complexes with perfluorinated carboxylates and tertiary phosphines [11–13]. Uncoordinated carboxylates can be detected in solution of sodium carboxylates of the analogous acids. Therefore, we have recorded  $^{19}\text{F}$  NMR of the equivalent sodium salts in acetonitrile solution, under the same conditions as used for complexes being studied (Table 2,  $\Delta_3$  and  $\Delta_5$ ). Resonances of the  $\text{C}_\alpha\text{F}_2$  fluorine in complexes **2–7**, and of  $\text{CF}_3$  for **1**, are shifted downfield ( $\Delta_3 = 0.4\text{--}1.7 \text{ ppm}$ ) in relation to those for sodium carboxylates. The coordination shift of  $\text{C}_\alpha\text{F}_2$  resonances can be taken as evidence of a  $\text{Cu-OOCR}$  bond, although it is difficult to correlate it with the mode of carboxylate binding.

Single, broad  $^{31}\text{P}$  ( $\Delta\nu_{1/2}$  ranging from  $230\text{--}1040 \text{ Hz}$ ) resonances in the spectra of complexes appeared in the range  $108.0\text{--}110.1 \text{ ppm}$ , which is  $20.6\text{--}22.7 \text{ ppm}$  upfield in relation to uncoordinated  $\text{P}(\text{OPh})_3$  (Table 2). The

upfield shift in  $^{31}\text{P}$  spectra favours the  $\pi$ -back donation from Cu(I) to phosphorus in tpp. The signal is not split, indicating that, in solution, the  $\text{CuP}_4$  moiety does not exist as a prevailing form or that a fast exchange reaction causes the lack of  $^{31}\text{P}$ – $^{63}\text{Cu}$  coupling. Exchange reactions present in solution can be studied using temperature-dependent  $^{31}\text{P}$  NMR spectra. We have recorded spectra in the 333–233 K range, expecting to find the coalescence temperature between different forms in solution. However, in the spectra of **2**, **5** and **7**, splitting of the phosphorus signal was not found.

The detection of a singlet suggests the appearance of at least two pseudotetrahedral species in equilibrium that averaged and broadened the signal [25–27]. Considering the above results, one can suggest coordination of triphenylphosphite along with bridging carboxylates and acetonitrile. The prevailing existing species can be described as isomers of  $[\text{Cu}(\text{CH}_3\text{CN})(\mu\text{-RCOO})\{\text{P}(\text{OPh})_3\}]$  (Fig. 1). This assumption may be explained by the fast exchange of  $\text{P}(\text{OPh})_3$ , and the lack of a favoured configuration with one phosphorus in the coordination sphere, which is typical for the large phosphine ligands such as triphenylphosphite [28] and triphenylphosphine ( $\text{PPh}_3$ ).

Table 3

$^{31}\text{P}$  and  $^{63}\text{Cu}$  NMR data of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$  ( $c=0.1$  m): $n\text{P}(\text{OC}_6\text{H}_5)_3$  system in acetonitrile solution

$n$	$^{63}\text{Cu}$ NMR		$^{31}\text{P}$ NMR	
	$\delta$ [ppm]	$\Delta\nu_{1/2}$ [Hz]	$\delta$ [ppm]	$\Delta\nu_{1/2}$ [Hz]
0.0	0.2	440	—	—
0.5	19.0	2560	108.9	1370
1.0	62.7	4680	106.5	1240
1.5	138.2	5300	109.7	680
2.0	141.0	7600	104.7	460
3.0	152.0	6360	117.6	280
4.0	145.1	6710	118.1	360
5.0	149.2	5080	118.3	160

We have checked the possibility of  $[\text{Cu}\{\text{P}(\text{OPh})_3\}_4]^+$  detection in the acetonitrile solution recording  $^{31}\text{P}$  NMR spectra for  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ :  $\text{P}(\text{OPh})_3$  system. The  $^{31}\text{P}$  single resonance lines for the systems  $\text{Cu}:n\text{P}(\text{OPh})_3$  from 1:0.5 to 1:5 were observed (Table 3). Even at the ratio 1:5, the resonance line from the uncoordinated  $\text{P}(\text{OPh})_3$  (130.7 ppm) was not found. Temperature-dependent spectra of solutions with M:L ratios of 1:1 and 1:4 were also investigated. In the 1:1 system, only an upfield shift of

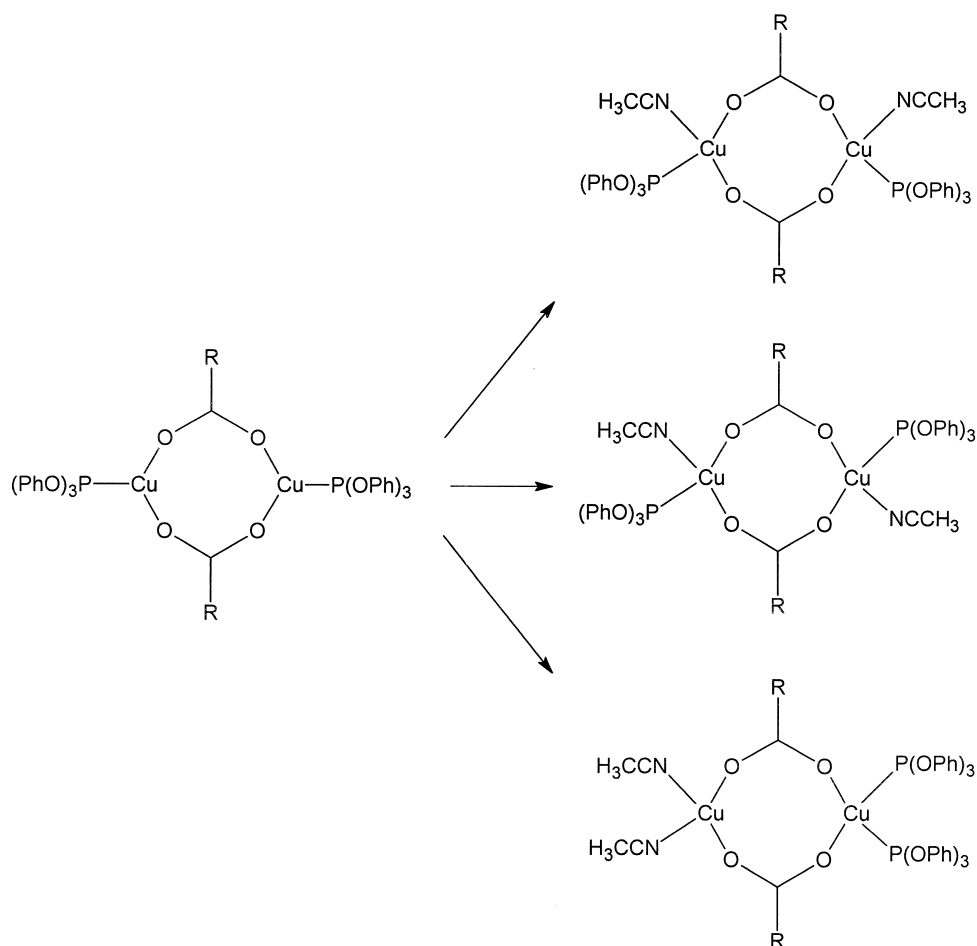


Fig. 1. Possible species existing in equilibrium after dissolving  $[\text{Cu}(\mu\text{-RCOO})\{\text{P}(\text{OPh})_3\}]_2$  in acetonitrile.

phosphite signals, with decreasing temperature, was observed. However, when the ratio of M:L was 1:4, the single phosphorus resonances that had been shifted downfield were detected, and these were split at 233 K into two lines (127.4 and 109.5 ppm) (Fig. 2). The latter was positioned at the same frequency as in the 1:1 system and was in a similar range as for complexes **1**, **4**, **5**, **6** and **7**. We can presume that this signal is from the species where one molecule of  $\text{P}(\text{OPh})_3$  is coordinated.

The main factors that influenced the  $^{63}\text{Cu}$  NMR signals were the quadrupolar relaxation of  $^{63,65}\text{Cu}$ , and the nature and rate of dynamic processes occurring in solution. These in turn were influenced by the temperature, distortions from the regular tetrahedral symmetry, and the electronic and steric properties of ligands. Studies of Cu(I) halide complexes [29–31] with phosphine ligands revealed that the dissociation of the complex in solution increased with ligand size, which, for tertiary phosphines, can be expressed by the Tolman cone angle. Furthermore,  $[\text{CuL}_4]\text{X}$  is regarded as a dominant species in solution [29,32–35], although in cases where there is an aromatic substituent on phosphines, several mononuclear and polynuclear complexes can also exist, i.e.,  $\text{CuL}_3\text{X}$ ,  $\text{CuL}_2\text{X}$  or  $\text{Cu}_2\text{L}_3\text{X}_2$ , depending on the coordinative properties of X [29]. Ligand exchange rates are usually too fast on the NMR time scale to identify individual species, except for very low temperatures. As reported, the extent of ligand dissociation in solution and the corresponding fast quadrupolar relaxation of the Cu nuclei in the low symmetry coordination resulted in a lack of  $^{63}\text{Cu}$  resonances [25].

$^{63}\text{Cu}$  spectra of the complexes revealed a broad singlet ( $\Delta\nu_{1/2}$  from 8150 to 22 520 Hz) in the range 64.2–150.0 ppm. In relation to complexes with  $\text{PR}_3$ , where R=Me or Et, they are shifted upfield and their frequency is closer to that of  $\text{PR}_{3-x}(\text{OR})_x$  ligands [36]. The  $^{63}\text{Cu}$  resonances reported for tetrahedral  $[\text{Cu}\{\text{P}(\text{OR})_3\}_4]\text{Cl}$  where R=Me or Et were found to be in the range 70–90 ppm [7,36] in the form of a quintet from Cu–P coupling, except for  $[\text{Cu}\{\text{P}(\text{OC}_6\text{H}_5)_3\}_4]\text{ClO}_4$ , for which the authors did not observe a  $^{63}\text{Cu}$  signal. To the best of our knowledge, the  $^{63}\text{Cu}$  resonances reported here are the first reported for Cu(I) complexes with triphenylphosphite. The expected spin–spin coupling  $^1J(^{31}\text{P}-^{63}\text{Cu})$  in  $^{63}\text{Cu}$  and  $^{31}\text{P}$  NMR spectra of the complexes under discussion was not detected. The lack of line-splitting can be caused by the fast exchange of  $\text{P}(\text{OC}_6\text{H}_5)_3$  and the low symmetry of the coordination centre. Considering the  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$  NMR and IR spectra results, one can assume a lower symmetry ( $\text{C}_{3v}$  or  $\text{C}_{2v}$ ) for the complexes studied in acetonitrile solution.

We have registered temperature-dependent  $^{63}\text{Cu}$  NMR spectra of **5** and **7** in the range 333–233 K (Table 4). Initially, the signals are shifted upfield, but, from 253 K, the reverse tendency is observed. The linewidth for **5** with a decrease in temperature expands followed by a significant decrease and a subsequent increase. In the case of **7**,

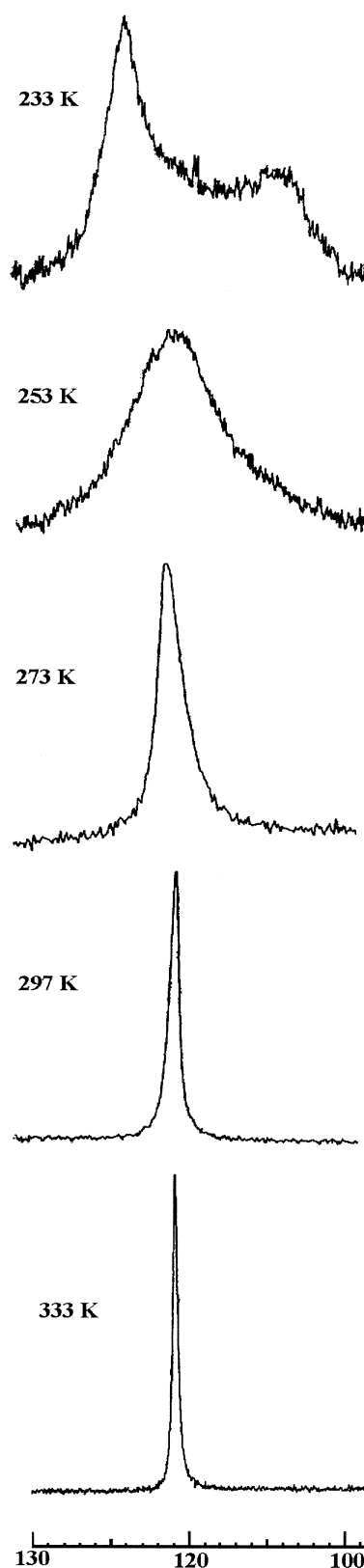


Fig. 2. Temperature-variable  $^{31}\text{P}$  NMR spectra of the  $[\text{Cu}(\text{CH}_3\text{CN})_4]\cdot\text{ClO}_4\cdot 4\text{P}(\text{OC}_6\text{H}_5)_3$  system in acetonitrile solution.

Table 4  
Temperature-variable  $^{63}\text{Cu}$  NMR spectra in acetonitrile solution

<i>T</i> [K]	(5) $[\text{Cu}(\mu\text{-C}_7\text{F}_{15}\text{COO})\text{-}\{\text{P}(\text{OPh})_3\}_2]$		(7) $[\text{Cu}(\mu\text{-C}_9\text{F}_{19}\text{COO})\text{-}\{\text{P}(\text{OPh})_3\}_2]$	
	$\delta$ [ppm]	$\Delta\nu_{1/2}$ [Hz]	$\delta$ [ppm]	$\Delta\nu_{1/2}$ [Hz]
333	—	—	94.9	6060
313	—	—	111.2	6130
297	112.1	13190	110.4	7240
273	111.2	14230	79.1	8150
253	146.2	5430	22.9	25 220
233	123.1	7500	50.7	18 880

$\Delta\nu_{1/2}$  increases up to 253 K and, afterwards, a reduction is observed. It should be added that, for **7** in the 333–297 K range, the chemical shift and linewidth changes are similar to those for the systems presented below without carboxylates. Below 297 K for **7**, and for **5** over the entire range of temperatures, the overall pattern of changes is different, most probably being caused by coordinated carboxylates in the studied system.

In the case of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4 \cdot n\text{P}(\text{OC}_6\text{H}_5)_3$ , where M:L=1:1, the relation of the  $^{63}\text{Cu}$  chemical shift to temperature was examined and a linear relationship (correlation coefficient  $R^2=0.9241$ ; straight line slope coefficient,  $-0.46$ ) was observed in the 333–273 K range, however, below 273 K, a slight deviation was detectable. The magnitude of the straight line slope coefficient reached a mean value between the systems with nitrogen donor ligands ( $-0.7$ ) and the complexes mentioned above of the type  $[\text{Cu}\{\text{P}(\text{OR})_3\}_4]\text{ClO}_4$  (ca.  $-0.1$ ), where R is an aliphatic substituent. An increase in the linewidth with a reduction in temperature (3880 Hz at 333 K to 17 200 Hz at 233 K) was also observed. For the system where M:L=1:4, the function  $\delta=f(T)$  at 273 K reached a

maximum, but at 233 K, it was impossible to determine the signal position due to the very strong line broadening that occurred. It should be added that resonance linewidths between 333–273 K are close to those obtained for M:L=1:1, but further cooling broadened the signals very rapidly. Bearing in mind that the  $^{63}\text{Cu}$  line appears only when the cation  $[\text{Cu}\{\text{P}(\text{OR})_3\}_4]^+$ , which undergoes fast chemical exchange is present in the solution, than with temperature decrease the reduction of the linewidth should be observed. In our system, the opposite effect was detected, that is, it favoured species with a symmetry lower than tetrahedral. We presume that our solution cannot be classified as a system with very fast quadruple relaxation, otherwise, simultaneously with the increase in the linewidth in  $^{63}\text{Cu}$  NMR, a rapid narrowing of the signal in  $^{31}\text{P}$  NMR should be observed.

### 3.3. Thermal analysis

Results of thermal analysis are listed in Table 5. Examination of the thermoanalytical curves suggests a two-stage, exothermic decomposition process of complexes **1**, **2** and **3** (Table 5). Analysis of the thermogravimetric (TG) curve indicates that, in the first step, decomposition of a carboxylic acid residue and one molecule of phosphite occurs, which is followed by dissociation of the second molecule of tpp. Decomposition reactions of **1**, **2** and **3** were completed in the range 618–653 K and the final product appeared to be a mixture of Cu,  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{P}_2\text{O}_7$  (3:1:1 for **1**; 1:1:1 for **2** and **3**). Powder diffractograms of the final products revealed lines for Cu, 0.181, 0.208 nm, and  $\text{Cu}_2\text{O}$ , 0.249, 0.215, 0.175, 0.151 nm, that correspond to those reported in the Powder Diffraction File [37]. IR spectra of the final product revealed strong

Table 5  
Results of thermal analysis (in nitrogen)

Compound	Heat effect	Temperature range [K]			Weight loss on TG [%]		Detached group	Final product $x\text{Cu}_2\text{O} : y\text{Cu}_2\text{O} : z\text{Cu}_2\text{P}_2\text{O}_7$
		$T_i^a$	$T_m^a$	$T_f^a$	Found	Calc.		
(1) $[\text{Cu}(\mu\text{-CF}_3\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2]$	exo	298	423	478	49.3	49.5	$\text{P}(\text{OC}_6\text{H}_5)_3$	3:1:1
	exo	478	568	618	32.2	31.9		
(2) $[\text{Cu}(\mu\text{-C}_2\text{F}_5\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2]$	exo	298	453	493	51.8	52.2	$\text{P}(\text{OC}_6\text{H}_5)_3$	1:1:1
	exo	493	533	653	29.1	28.9		
(3) $[\text{Cu}(\mu\text{-C}_3\text{F}_7\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2]$	exo	298	458	488	56.0	56.3	$\text{P}(\text{OC}_6\text{H}_5)_3$	1:1:1
	exo	488	548	653	26.7	26.4		
(4) $[\text{Cu}(\mu\text{-C}_6\text{F}_{13}\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2]$	exo	298	<sup>b</sup>	413	17.5		$\text{P}(\text{OC}_6\text{H}_5)_3$	1:1:1
	exo	413	473	498	48.4	65.2		
	exo	498	553	643	20.6	21.0		
(5) $[\text{Cu}(\mu\text{-C}_7\text{F}_{15}\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2]$	exo	313	<sup>b</sup>	428	19.0		$\text{P}(\text{OC}_6\text{H}_5)_3$	1:1:1
	exo	428	478	508	47.9	67.4		
	exo	508	538	643	19.7	19.7		
(6) $[\text{Cu}(\mu\text{-C}_8\text{F}_{17}\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2]$	exo	298	<sup>b</sup>	418	20.6		$\text{P}(\text{OC}_6\text{H}_5)_3$	1:1:1
	exo	418	473	503	46.7			
	exo	503	548	638	20.6	87.9		
(7) $[\text{Cu}(\mu\text{-C}_9\text{F}_{19}\text{COO})\{\text{P}(\text{OC}_6\text{H}_5)_3\}_2]$	exo	303	473	708	88.1	88.6		1:1:1

<sup>a</sup>  $T_i$ , initial temperature;  $T_m$ , maximum temperature;  $T_f$ , final temperature.

<sup>b</sup> Unable to determine.

vibrations in the range 1065–1071  $\text{cm}^{-1}$  that were characteristic for  $\text{Cu}_2\text{P}_2\text{O}_7$  [38]. Similar final products were reported for other copper(I) phosphine complexes, e.g.  $[\text{Cu}\{\text{P}(\text{C}_6\text{H}_5)_3\}_4]\text{BF}_4$  [39]. Complexes **4**, **5** and **6** decompose in three exothermic processes and the final product is the same mixture as for **2** and **3**. For **1–5**, the results of analysis of TG curves are in favour of tpp detachment in the second stage. The onset temperatures of the consecutive stages for **6** are very close; therefore, the total mass loss on the TG curve was taken as evidence of tpp and carboxylate dissociation. Complex **7** decomposed in a single stage to the same mixture as for **2–6**. The onset temperature of the first exotherm is in the range 298–313 K, suggesting that the perfluorinated chain had a small influence on the thermal stability of the complexes studied. The temperatures of the final product formation are in the range acceptable for CVD purposes with the hot wall reactor (625 K). The final products of complex decomposition are discouraging for use in the CVD of copper or copper oxide films, however, the complexes are volatile viscous liquids and can decompose in different ways under conditions applied for CVD or other deposition techniques.

#### 4. Conclusions

These results show that neat isolated complexes can be regarded as trigonal dimeric species with bridging carboxylates and triphenylphosphite of general formula  $[\text{Cu}(\mu\text{-RCOO})\{\text{P}(\text{OPh})_3\}]_2$ . This type of complexation is different from tetrameric [40] or polymeric [41] structures found for Cu(I) carboxylates in the solid state [42]. Trigonal geometry was found for dimeric Cu(I) halide complexes with triphenylphosphine, but, to the best of our knowledge, not for triphenylphosphite. In our complexes, the bridging carboxylates favour dimer formation. Analysis of  $^{63}\text{Cu}$  NMR spectra suggests the fast exchange of tpp in acetonitrile solution in the range 333–233 K. Copper relaxation is sufficiently slow to record the signal, which can most probably be related to the bridging carboxylates. The complexes examined are the first systems with tpp where  $^{63}\text{Cu}$  resonances were observed. This is a rare example of complexes with a geometry lower than  $T_d$ , for which  $^{63}\text{Cu}$  signals have been registered. In Cu(I) complexes with carboxylates and monodentate phosphine, only the chelating mode of carboxylate was noticed [3], but the bridging mode seems to be characteristic for tertiary phosphites.

#### Acknowledgements

Financial support from the Polish Committee for Scientific Research (KBN) is gratefully acknowledged, grant PB 619/T09/97/13. The authors wish to thank Z. Hupenthal (N.C.U.) for  $^{31}\text{P}$ ,  $^{63}\text{Cu}$  NMR measurements and W.

Ciesielski (Center for Macromolecular Research, Łódź) for recording temperature-dependent NMR spectra.

#### References

- [1] D.J. Darensbourg, M.W. Holtcamp, E.M. Longridge, K. Klausmeyer, J.H. Reibenspies, *Inorg. Chim. Acta* 227 (1994) 223.
- [2] D.A. Edwards, R. Richards, *J. Chem. Soc., Dalton Trans.* 7 (1975) 637.
- [3] R.D. Hart, P.C. Healy, G.A. Hope, D.W. Turner, A.H. White, *J. Chem. Soc., Dalton Trans.* 5 (1994) 773.
- [4] R.L. Beddoes, J.A. Connor, D. Dubowski, A.C. Jones, O.S. Milles, R. Price, *J. Chem. Soc., Dalton Trans.* 10 (1981) 2119.
- [5] D.F. Shriver, P.W. Atkins, C.H. Langford (Eds.), *Inorganic Chemistry*, Oxford University Press, Oxford, 1994, pp. 212–216.
- [6] C.A. Tolman, *Coord. Chem. Rev.* 77 (1977) 313.
- [7] P. Granger, in: P.S. Pregosin (Ed.), *Transition Metal Nuclear Magnetic Resonance*, Elsevier, Amsterdam, 1991, pp. 265–273.
- [8] B. Mohr, E.E. Brooks, N. Rath, E. Deutsch, *Inorg. Chem.* 30 (1991) 4541.
- [9] S.J. Berners-Price, C. Brevard, A. Pagelot, P.J. Sadler, *Inorg. Chem.* 25 (1986) 596.
- [10] S.J. Berners-Price, L.A. Colquhoun, P.C. Healy, K.A. Byriel, J.V. Hanna, *J. Chem. Soc., Dalton Trans.* (1992) 3357.
- [11] E. Szlyk, I. Lakomska, A. Grodzicki, *Polish J. Chem.* 68 (1994) 1529.
- [12] E. Szlyk, I. Lakomska, A. Grodzicki, *Polish J. Chem.* 69 (1995) 1103.
- [13] E. Szlyk, I. Lakomska, A. Grodzicki (Eds.), *Trends in Coordination Chemistry*, Slovak Technical University Press, 1995, p. 151.
- [14] D.L. Schultz, T.J. Marks, *Adv. Mater.* 6 (1994) 719.
- [15] V.G. Minkina, *Russ. Chem. Bull.* 42 (1993) 1461.
- [16] K. Nakamoto (Ed.), *Infrared, Raman Spectra of Inorganic, Coordination Compounds*, Wiley & Sons, New York, 1986, p. 233.
- [17] G.B. Deacon, R.J. Phillips, *Coord. Chem. Rev.* 33 (1980) 227.
- [18] N.F. Curtis, *J. Chem. Soc. (A)* (1968) 1579.
- [19] Atlas IR-Spektrov fosforoorganicheskikh soedinenij, Moskva, 1977, p. 237.
- [20] V.I. Kurashov, D.G. Pobiedimskij, P.A. Kirpichnikov, *Doklady Akad. SSSR* 238 (1978) 1407.
- [21] V.I. Kurashov, D.G. Pobiedimskij, *Koord. Khim.* 5 (1979) 1162.
- [22] D.A. Edwards, R. Richards, *Spectrochim. Acta* 34A (1978) 167.
- [23] R.L. Keiter, J.G. Verkade, *Inorg. Chem.* 9 (1970) 404.
- [24] G.A. Bowmaker, R.D. Hart, B.E. Jones, B.W. Skeleton, A.H. White, *J. Chem. Soc., Dalton Trans.* 24 (1995) 3063.
- [25] A. Marker, M.J. Gunter, *J. Magn. Reson.* 47 (1982) 118.
- [26] S. Kitagawa, M. Munakata, M. Sasaki, *Inorg. Chim. Acta* 120 (1) (1986) 77.
- [27] D.G. Pobiedimskij, D. Szeller, T.N. Kondratieva, V.I. Kurashov, P.A. Kirpichnikov, *Doklady Akad. SSSR* 250 (1980) 661.
- [28] J.R. Black, W. Levason, M.D. Spicer, M. Webster, *J. Chem. Soc., Dalton Trans.* 20 (1993) 3129.
- [29] S.J. Lippard, J.J. Mayerle, *Inorg. Chem.* 11 (1972) 753.
- [30] D.J. Fife, W.M. Moore, K.M. Morse, *Inorg. Chem.* 21 (1984) 1684.
- [31] E.L. Muetterties, C.W. Alegranti, *J. Am. Chem. Soc.* 92 (1970) 4114.
- [32] P.S. Pregosin, R.W. Kunz,  $^{31}\text{P}$ ,  $^{13}\text{C}$  NMR of Transition Metal Complexes, Springer-Verlag, Berlin, 1979.
- [33] J.T. Gill, J.J. Mayerle, P.S. Weleker, D.F. Lewis, D.A. Ucko, D.J. Barton, D. Stowens, S.J. Lippard, *Inorg. Chem.* 15 (1975) 1155.
- [34] A.P. Gaughan, Z. Dori, J.A. Ibers, *Inorg. Chem.* 13 (1974) 1657.
- [35] M.B. Dines, *Inorg. Chem.* 11 (1972) 2949.
- [36] P. Kroneck, O. Lutz, A. Nolle, H. Oehler, *Z. Naturforsch.* 35a (1979) 221.

- [37] Powder Diffraction File, Sets 4-836, 5-667, 22-1090; Joint Committee on Diffraction Standards, 1977.
- [38] R.A. Nyquist, R.O. Kagel (Eds.), *Infrared Spectra of Inorganic Compounds*, Academic Press, New York, 1971, pp. 186–187.
- [39] V.A. de Lucca Neto, A.E. Mauro, V. Sargentelli, M. Ionashiro, *Thermochim. Acta* 260 (1995) 235.
- [40] M.G.B. Drew, D.A. Edwards, D.A. Richards, *J. Chem. Soc., Dalton Trans.* 3 (1977) 299.
- [41] M.G.B. Drew, D.A. Edwards, D.A. Richards, *J. Chem. Soc., Chem. Commun.* 4 (1973) 124.
- [42] T.P. Lockhart, D.A. Haitko, *Polyhedron* 4 (1985) 1745.