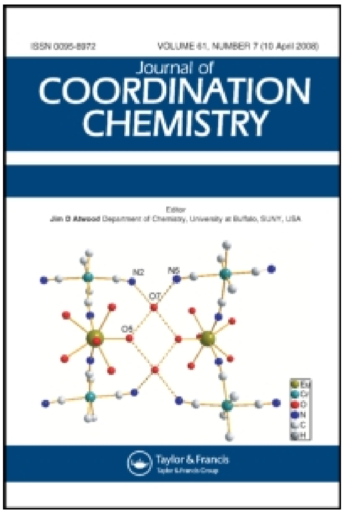

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Szłyk, Edward , Kucharek, Robert and Szymańska, Iwona(2001) 'VARIABLE-TEMPERATURE ^{31}P AND ^{63}Cu NMR AND MASS SPECTROSCOPIC CHARACTERISATION OF NEW COPPER(I) PERFLUORINATED CARBOXYLATE COMPLEXES WITH 1,2-BIS(DIPHENYLPHOSPHINE)ETHANE', Journal of Coordination Chemistry, 53: 1, 55 — 67

To link to this Article: DOI: 10.1080/00958970108022601

URL: http://dx.doi.org/10.1080/00958970108022601

J. Coord. Chem., 2001, Vol. 53, pp. 55–67
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Printed in Malaysia.

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(Received 7 March 2000)

Copper(I) perfluorinated carboxylates complexes with 1,2-bis(diphenylphosphine)ethane (dppe) of general formula $[Cu_2(dppe)_2(\mu-RCOO)_2]$ and $[Cu(dppe)_2](RCOO)$ $R = C_2F_5$, C_4F_9, C_6F_{13} have been prepared and characterised by vibrational and mass spectra in the solid state and with ^{13}C, ^{19}F NMR and variable temperature ^{31}P, ^{63}Cu NMR spectra in solution. Monomeric forms can be proposed for complexes with M : L = 1 : 2, and dimeric for M : L = 1 : 1. Temperature variable ^{31}P NMR spectra revealed the species $[Cu_2(dppe)_2(\mu-RCOO)_2]$, $[Cu_2(dppe)_2(RCOO)]^+$, $[Cu(RCOO)(dppe)]$, $[Cu(dppe)_2]^+$ in equilibrium. Analysis of IR and mass spectra suggests bridging carboxylates in $[Cu_2(dppe)_2(\mu-RCOO)_2]$ and ions in $[Cu(dppe)_2](RCOO)$.

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

INTRODUCTION

Copper(I) complexes with oxygen donor ligands exist in mono- or multinuclear structures depending on the secondary ligands in the coordination sphere [1–4].

Copper(I) carboxylates complexes are less studied than Cu(II) analogues due to the instability of the Cu(I)–O bond. One can explain this as being the

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result of a weak bond between hard oxygen atoms and soft copper(I) [5]. Moreover, Cu(I) perfluorinated carboxylates are much less studied than aliphatic analogues because oxygen atoms reveal lower σ-donor properties, thus causing further destabilisation of the Cu—O bond. Hence one may presume that they could be coordinated in a different way, resulting in new and interesting structures. In addition, structural features of copper(I) complexes depend on the σ-donor and π-acceptor properties of the secondary ligand. Consequently 1,2-bis(diphenylphosphine)ethane (dppe) has been chosen because it demonstrates strong π-acceptor properties with additional stabilisation coming from chelation [6–8]. It has been reported that cytotoxicity and antitumour activity of dppe and related phosphines are enhanced when these ligands are complexed with Cu(I) [9–11]. They may find also use as starting materials for radiopharmaceuticals and Positron Emission Tomography [12, 13]. Therefore the main purpose of the presented work was the isolation of new Cu(I) complexes, and characterisation with ^{13}C, ^{19}F, ^{31}P, ^{63}Cu NMR, vibrational and mass spectra. Good NMR sensitivities of ^{63}Cu and ^{65}Cu are in favour of NMR, but the significant quadrupole moments of these nuclei limit the number of copper resonances that have been observed in solution [14–17]. In this paper we report further examples of ^{63}Cu NMR resonances.

EXPERIMENTAL

Chemicals

Copper powder for organic synthesis, perfluorinated carboxylic acids (97–99%) and dppe (97%) were purchased from Aldrich and used without further purification. Acetonitrile and methylene chloride (Aldrich) were dried by standard methods. $CuCO_3 \cdot Cu(OH)_2 \cdot nH_2O$ was purchased from POCh (Poland, Gliwice) and used as received. Copper(II) carboxylates $Cu(RCOO)_2$, where $R = C_2F_5$, C_4F_9, C_6F_{13} were obtained by reaction of a slight excess of basic copper(II) carbonate with the respective carboxylic acid in water or water–ethanol (10 : 1) solution, and their stoichiometry was proven by metal determination and IR spectra.

Instrumentation

NMR spectra were recorded with a Varian Gemini 200 MHz instrument: ^{13}C at 50 MHz and TMS as standard; ^{19}F at 188 MHz, standard $CFCl_3$;

^{31}P at 80.95 MHz, standard 80% H_3PO_4; ^{63}Cu at 56.79 MHz, standard $[Cu(CH_3CN)_4]ClO_4$; $CDCl_3$ was used as solvent. The Concentration of complexes for ^{63}Cu NMR measurements was 0.02 mol dm^{-3}. Temperature-dependent ^{31}P and ^{63}Cu NMR spectra were measured with a Bruker 300 MSL spectrometer in $CDCl_3$, between 295–225 K. To examine the linewidth of peaks, no baseline correction or apodization function was used in the data processing. Linewidths were measured using manual optimisation within the peak search module. The error in linewidth measurements was assumed to be equal to the digital resolution (1.95 Hz). IR spectra were recorded with a Spectrum 2000 Perkin Elmer FT-IR spectro photometer in the range 4000–400 cm^{-1} using KBr discs, and 700–100 cm^{-1} using polyethylene discs. Copper was determined with a Carl Zeiss Jena AAS spectrophotometer. Mass spectra were recorded using an AMD-640 mass spectrometer. The LSIMS ionisation method using NBA alcohol as liquid matrix was applied.

Syntheses

Complexes of general formula $[Cu(dppe)_2](RCOO)$ and $[Cu_2(dppe)_2(\mu\text{—}RCOO)_2]$ where $R = C_2F_5$, C_4F_9, C_6F_{13} were prepared as follows. Copper(II) perfluorinated carboxylates (0.8 mmol) dissolved in 20 cm^3 of acetonitrile were placed in a Schlenk tube, followed by excess copper powder (0.5 g, 8 mmol). The resulting suspension was stirred under argon until the solution became colourless, then dppe (1.6 mmol in the case of M : L = 1 : 1 or 3.2 mmol for M : L = 1 : 2) in 20 cm^3 of methylene chloride was added in one portion. The reaction mixture was stirred for 12 h, filtered and evaporated on a vacuum line to afford yellow or colourless crystals. The results of element analyses are as follows [% (calc./found)]: (**1**) $C_{58}H_{48}Cu_2F_{10}O_4P_4$, Cu (10.2/9.9), C (55.7/55.9), H (3.9/4.3); (**2**) $C_{55}H_{48}CuF_5O_2P_4$, Cu (6.2/6.1), C (64.5/64.7), H (4.7/5.2); (**3**) $C_{62}H_{48}Cu_2F_{18}O_4P_4$, Cu (8.8/8.5), C (51.4/51.1), H (3.3/3.6); (**4**) $C_{57}H_{48}CuF_9O_2P_4$ Cu (5.7/5.4), C (60.9/60.6), H (4.3/4.5); (**5**) $C_{59}H_{48}CuF_{13}O_2P_4$ Cu (5.2/5.1), C (57.9/57.9), H (4.0/4.4).

RESULTS AND DISCUSSION

Mass Spectrometry

In order to confirm the stoichiometry of the complexes and the fragmentation mechanism the LSIMS spectra were recorded. Because the natural abundance of copper is ^{63}Cu (69.1%) and ^{65}Cu (31.9%), compounds which have one copper atom give two signals with 2:1 intensity. Species with two copper atoms should reveal three peaks with the characteristic 4:4:1 intensity pattern. Mass spectra point towards the following fragments (*m*/*z*) (relative intensity, %): (**1**) 461 $[Cu(dppe)]^+$ (100%), 859 $[Cu(dppe)_2]^+$ (94%), 687 $[Cu_2(dppe)(C_2F_5COO)]^+$ (42%), 624 $[Cu(dppe)(C_2F_5COO)]^+$ (14%), 1085 $[Cu_2(dppe)_2(C_2F_5COO)]^+$ (6%); (**2**) 859 $[Cu(dppe)_2]^+$ (100%), 461 $[Cu(dppe)]^+$ (92%); (**3**) 461 $[Cu(dppe)]^+$ (100%), 859 $[Cu(dppe)_2]^+$ (70%), 787 $[Cu_2(dppe)(C_4F_9COO)]^+$ (45%), 1185 $[Cu_2(dppe)_2(C_4F_9COO)]^+$ (25%), 724 $[Cu(dppe)(C_4F_9COO)]^+$ (15%); (**4**) 859 $[Cu(dppe)_2]^+$ (100%), 461 $[Cu(dppe)]^+$ (100%), 724 $[Cu(dppe)(C_4F_9COO)]^+$ (5%); (**5**) 461 $[Cu(dppe)]^+$ (100%), 859 $[Cu(dppe)_2]^+$ (75%), 824 $[Cu(dppe)(C_6F_{13}COO)]^+$ (5%). The presence of the ion fragment 687 *m*/*z* in the spectrum of **1** (Fig. 1) is in favour of the dimeric fragment $[Cu_2(dppe)(C_2F_5COO)]^+$. Characteristic signal intensities confirms the existence of two copper ions in the latter fragment. The lack of the molecular ion is thought to be caused by the high instability of $[Cu_2(dppe)_2(\mu-C_2F_5COO)_2]$.

The most pronounced peaks can be related to two characteristic ionic fragments $[Cu(dppe)_2]^+$ and $[Cu(dppe)]^+$, 461 and 859 *m*/*z*, respectively. In the spectrum of **5**, the ion peak (1178 *m*/*z*) was detected, assigned to $[Cu(dppe)(C_6F_{13})]^+$. This fragment is in favour of the carboxylate degradation process, which is more pronounced in complexes with long

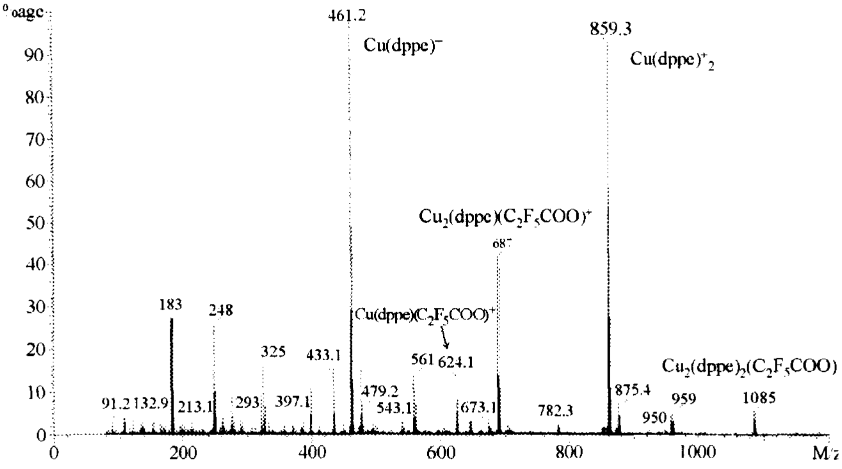

FIGURE 1 LSIMS mass spectrum of **1** $[Cu_2(dppe)_2(\mu-C_2F_5COO)_2]$.

chains. That may be the main reason for the lack of molecular peaks in the spectra of the complexes under discussion. Analysis of peak intensities can be rationalized with the following fragmentation scheme (Fig. 2).

Results are in favour of dimeric species for **1** and **3**, whereas **2**, **4** and **5** are most probably monomeric.

NMR Spectroscopy

NMR analyses are very useful to elucidate the solution structure of the complexes, which should be compared with solid-state structures. ^{13}C, ^{19}F, ^{31}P, ^{63}Cu resonances were assigned and are listed in Table I. ^{13}C resonances of COO carbon were observed as weak signals (158.8–161.0 ppm) shifted downfield in comparison to the free acids (Tab. I). In the case of **4** and **5** they are split into triplets due to spin–spin coupling [$^2J(^{13}\mathrm{C}-^{19}\mathrm{F}) = 20.4-23.5\,\mathrm{Hz}$]. The chemical shifts of COO carbon are very similar, within the studied series of complexes, indicating that their coordination modes may be related. The magnitude of COO coordination shift ($\Delta\delta_{\mathrm{COO}}$) is small (0.6–2.0 ppm), but more than twice the value observed for Cu(I) carboxylate complexes with tertiary phosphites [18]. On the other hand these values are comparable to that found in the spectra of Ag(I) and Au(I) complexes with triphenylphosphine. Such magnitudes of the ^{13}C COO coordination shift appear to be a general feature for Au(I) and Ag(I) complexes with tertiary

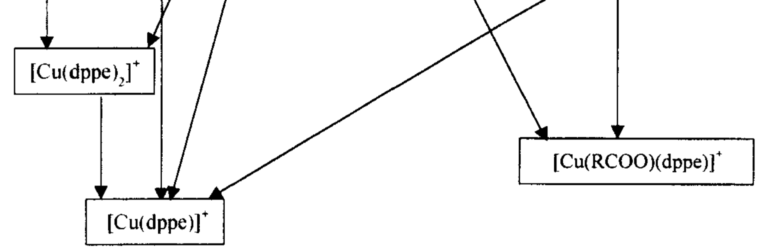

FIGURE 2 Fragmentation scheme for the dimeric complexes $[\mathrm{Cu_2(dppe)_2(\mu-}R\mathrm{COO)_2}]$.

TABLE I ^{13}C, ^{19}F, ^{31}P, ^{63}Cu NMR data [ppm] for the complexes

	^{13}C			^{19}F		^{31}P		^{63}Cu	
Complex	δCH_2	δCOO	$\Delta\delta_{COO}$	$\delta CF_{2\alpha}$	$\Delta\delta_{F\alpha}$	$\delta^{31}P$	$\Delta\delta_P$	$\delta^{63}Cu$	$\Delta\nu_{1/2}[Hz]$
1 $[Cu_2(dppe)_2(\mu-C_2F_5COO)_2]$	23.4	158.8	0.6	−41.5 (S)	3.4	−6.0	6.0	139.1	4000
2 $[Cu(dppe)_2](C_2F_5COO)$	26.5	161.1	2.9	−41.8 (S)	3.1	7.2	19.2	137.8	6050
3 $[Cu_2(dppe)_2(\mu-C_4F_9COO)_2]$	[a]	[a]	–	−39.0 (S)	3.0	6.3	18.3	[a]	[a]
4 $[Cu(dppe)_2](C_4F_9COO)$	26.7	161.0	1.5	−38.7 (T)[b]	3.3	5.8	17.8	143.5	4800
5 $[Cu(dppe)_2](C_6F_{13}COO)$	26.6	161.0	2.0	−38.5 (T)[c]	3.4	6.9	18.9	145.8	4900

$\Delta\delta_{F\alpha} = \delta_{complex} - \delta_{acid}$, $\Delta\delta_F = \delta_{complex} - \delta_{acid}$, $\Delta\delta_{COO} = \delta_{complex} - \delta_{acid}$, $\Delta\delta_P = \delta_{complex} - \delta_{dppe}$, $\delta_{dppe} = -12.0$ ppm; S – singlet, T – triplet; [a] Unobservable in the ^{63}Cu NMR due to the fast quadrupole relaxation; [b] $^4J(F\text{-}F) = 11.6$ Hz; [c] $^4J(F\text{-}F) = 12.8$ Hz.

phosphines and bidentate carboxylates [19–21]. Moreover the COO coordination shift is more pronounced for the present compounds, than observed for analogous Cu(I) complexes with $P(OR)_3$ [18]. The magnitude of the coordination shift suggests the bridging mode of carboxylate complexation. One set of phenyl carbon resonances is observed for dppe, which suggest that the phenyl groups are on the same side of the metal ions in a symmetrical arrangement with respect to the ligand, otherwise the phenyl groups would be diastereotopic. The ^{13}C signal for $—CH_2—$ was detected as a broad singlet in the range 23.4–26.7 ppm (Tab. I), also in favour of a symmetrical arrangement of the phenyl groups.

In ^{19}F NMR spectra the most distinct changes were observed for $C_\alpha F_2$ signals, which are shifted downfield $\Delta\delta_{F\alpha} = 3.0-3.4$ ppm in relation to the free carboxylic acids (Tab. I). Analogous effects were found in ^{19}F NMR spectra of Cu(I), Ag(I), Au(I) complexes with perfluorinated carboxylates and tertiary phosphines [18–21]. The coordination shift of $C_\alpha F_2$ can be seen as additional evidence of carboxylate complexation in solution. Coordination shifts of $C_\alpha F_2$ detected in the spectra of the complexes are similar to those observed for analogous compounds with tertiary phosphites [18]. This can be related to carboxylate complexation, although it is difficult to correlate this with the mode of carboxylate binding.

^{31}P NMR spectra of the complexes exhibit at ambient temperature a broad line ($\Delta\nu_{1/2} = 202-1417$ Hz) in the 5.8–7.2 ppm range, shifted downfield in relation to free dppe (Tab. I). Calculated coordination shifts $\Delta\delta_P = 17.8-19.2$ ppm (except for **1** where $\Delta\delta = -6.0$ ppm) are similar to that reported by van Koten [22] for dinuclear silver(I) carboxylato complexes with dppm. The interpretation of ^{31}P shifts is difficult due to such effects as variability of σ- and π-contributions to the metal–phosphorous bond, the other coordinated ligands and complex geometry. The relatively large linewidth of ^{31}P NMR resonances in the spectra of **2**, **4** and **5** may be caused by slight deformation of the $[CuP_4]^+$ cation characteristic for diphosphine or by chemical exchange of the dppe ligand (signal at − 9 ppm). On the other hand, for dimeric compounds **1** and **3** the detected signal shapes can be related to the following species existing in equilibrium: $[Cu_2(dppe)_2(\mu—RCOO)_2]$, $[Cu(dppe)_2]^+$, $[Cu_2(dppe)_2(RCOO)]^+$, $[Cu(dppe)(RCOO)]$.

In order to confirm the above hypothesis we have measured variable temperature ^{31}P NMR spectra of **1**, **2**, **4**, and **5** between 323–223 K. Spectra of **1** at 323 K revealed a strong signal (−5.4 ppm) which upon temperature decrease splits into 3 bands centred at 7.8, −5.5 and −0.6 ppm (Fig. 3). The signal at 7.8 ppm can be assigned to $[Cu(dppe)_2]^+$, [23] the strongest at

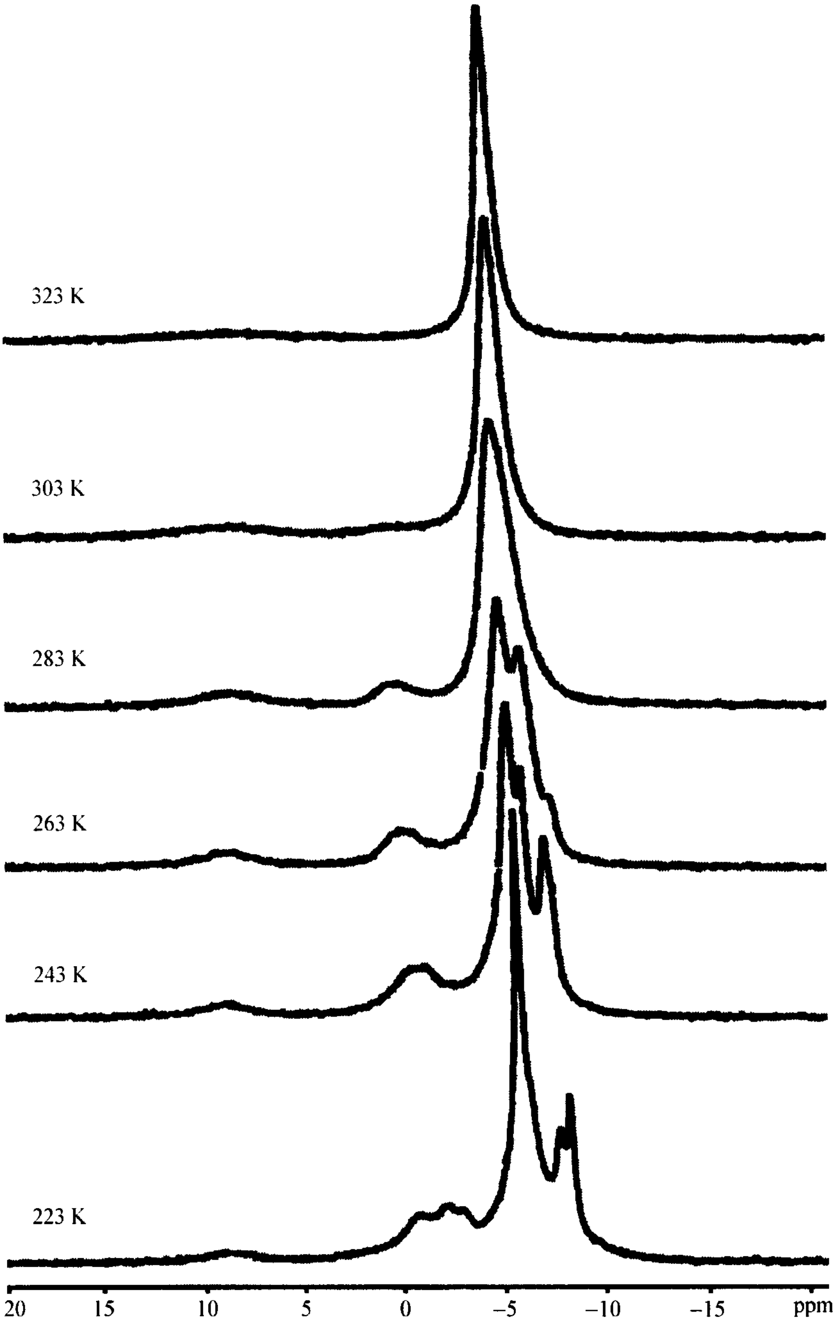

FIGURE 3 Temperature dependent ^{31}P NMR spectra of **1**, $[Cu_2(dppe)_2(\mu-C_2F_5COO)_2]$.

-5.5 ppm to $[Cu_2(dppe)_2(\mu - RCOO)_2]$, $[Cu(dppe)(RCOO)]$, and that at -0.6 ppm to the $[Cu_2(dppe)_2(RCOO)]^+$ dimer. Further decrease of temperature (263 K), caused the appearance of the free dppe signal at -7.7 ppm which at 243 K became distinctly separated (Fig. 3). From this observation we conclude that with temperature decrease the rate of the chemical exchange reaction is reduced.

Spectra of **2**, **4** and **5** at temperatures exhibit two signals, which can be assigned to $[Cu(dppe)_2]^+$ (~ 6 ppm) and free dppe (~ -10 ppm) [6, 7, 24]. These signals with temperature decrease to 223 K were shifted slightly to lower field (0.5 ppm) and became broader, but no coalescence of signals was observed. We conclude that in $CDCl_3$ solution the dominating form is $[Cu(dppe)_2]^+$ (Fig. 4). The exchange of dppe was slow on the NMR time scale, because the dppe signal was noted (Fig. 4). Results of ^{13}C and ^{19}F NMR analyses are in favour of diphosphine replacement by the carboxylate. In this case the existence of a minor population of moieties similar to those present in solutions of **1** and **3** can be suggested.

The temperature dependence of the NMR line shapes observed in ^{63}Cu NMR spectra can be interpreted in terms of the quadrupolar relaxation

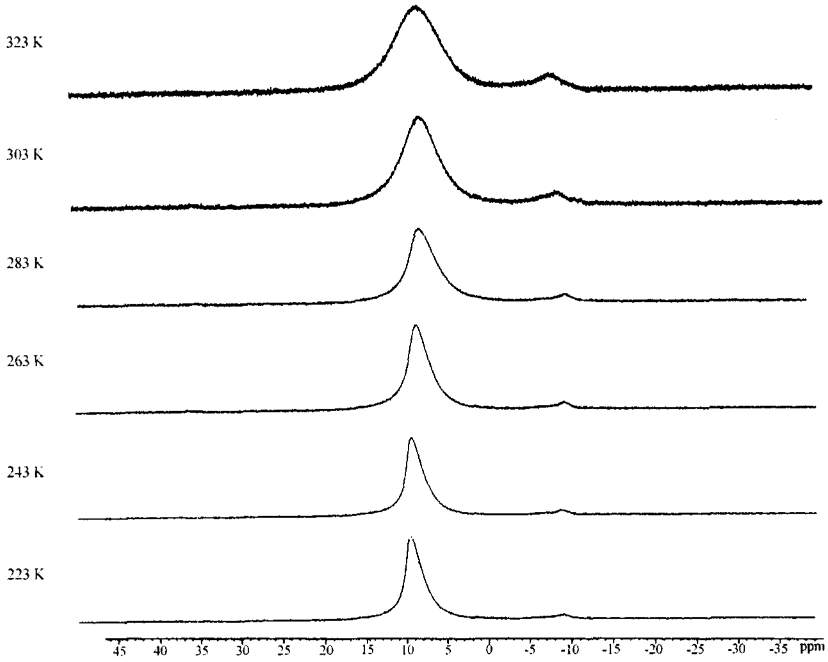

FIGURE 4 Temperature dependent ^{31}P NMR spectra of **2**, $[Cu(dppe)_2](C_2F_5COO)$.

arising from ^{63}Cu and ^{65}Cu [23]. Effects of the quadrupolar relaxation on the NMR line shapes have been discussed in detail by several authors [25–27]. Both copper isotopes have relatively large quadrupolar moments and they couple strongly by means of molecular reorientation to cause the collapse of the multiplet structure as temperature is decreased. Temperature lowering provides a greater quadrupolar contribution of the copper centre to the spin relaxation process. This results in collapse of the ^{31}P quartet and the ^{63}Cu quintet at low temperatures. The ^{63}Cu NMR resonance of **2** at 298 K appears as a broad signal centred at 138 ppm ($\Delta\nu_{1/2} = 6050$ Hz), which become broader with temperature decrease (273 K $-\Delta\nu_{1/2} = 7160$ Hz; 253 K $-\Delta\nu_{1/2} = 11300$ Hz; 223 K $-\Delta\nu_{1/2} = 11380$ Hz; Fig. 5). Observed shapes of signals are in favour of effective quadrupolar relaxation even at ambient temperatures, which can be related to lower than T_d symmetry of the coordination sphere for the species $[Cu(dppe)_2]^+$, $[Cu_2(dppe)_2(\mu-RCOO)_2]$, $[Cu_2(dppe)_2(RCOO)]^+$, $[Cu(dppe)(RCOO)]$.

IR Spectra

Carboxylates coordinate to metal ions in many ways, as uni- or bidentates (bridging or chelating), [28–30] as concluded from analysis of COO asymmetrical and symmetrical stretching vibrations. For the studied complexes these bands were detected in the range $\nu_a COO = 1694-1686\,cm^{-1}$ and $\nu_s COO = 1415-1410\,cm^{-1}$.

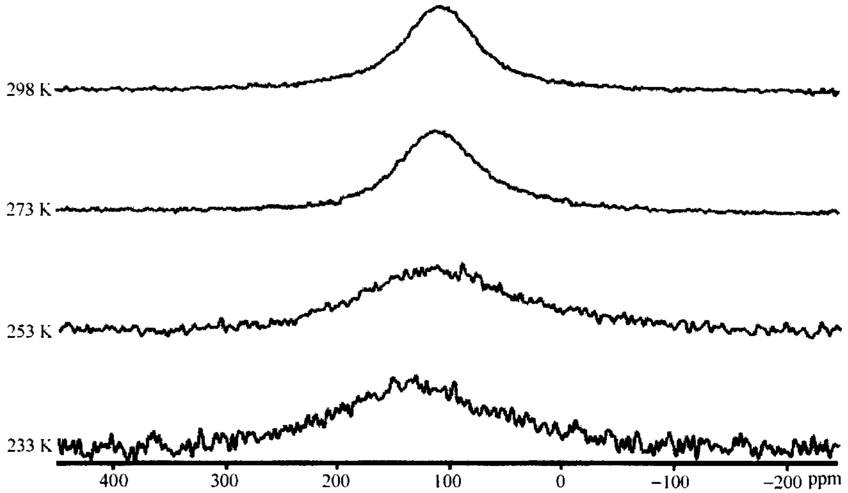

FIGURE 5 Temperature dependent ^{63}Cu NMR spectra of **2**, $[Cu(dppe)_2](C_2F_5COO)$.

TABLE II IR data [cm^{-1}] for the complexes

Complex	$\nu_a COO$	$\nu_s COO$	$\Delta\nu$	$\Delta\nu_1$	$\nu_a Cu—O$	$\nu_s Cu—O$	$\nu_a Cu—P$	$\nu_s Cu—P$
1 $[Cu_2(dppe)_2(\mu—C_2F_5COO)_2]$	1690	1415	275	268	318	243	161	131
2 $[Cu(dppe)_2](C_2F_5COO)$	1693	1413	280	268	[a]	[a]	158	128
3 $[Cu_2(dppe)_2(\mu—C_4F_9COO)_2]$	1686	1413	273	270	326	248	153	123
4 $[Cu(dppe)_2](C_4F_9COO)$	1694	1414	280	270	[a]	[a]	156	121
5 $[Cu(dppe)_2](C_6F_{13}COO)$	1693	1410	283	272	[a]	[a]	152	123

$\Delta\nu = \nu_a COO - \nu_s COO$ for complex, $\Delta\nu_1 = \nu_a COO - \nu_s COO$ for sodium carboxylates; [a] Not detected due to ionic carboxylates in **2**, **4** and **5**.

As a criterion of carboxylate binding mode we have applied the parameter $\Delta\nu = \nu_{\text{asym}} - \nu_{\text{sym}}$ [2, 28, 29]. Estimation of the nature of carboxylate linkage with a metal ion is based on the relation between the $\Delta\nu$ value calculated for the complex and $\Delta\nu_{\text{COO}}$ found in the sodium carboxylate. Values of $\Delta\nu$ (273–283 cm^{-1}) calculated for **1** and **3**, compared to $\Delta\nu$ for the appropriate sodium carboxylates are in favour of bridging coordination but for complexes **2**, **4**, **5**, carboxylates are ionic (Tab. II). Spectra in the range of metal–ligand vibrations revealed bands which can be assigned to Cu—O(*R*COO) and Cu—P stretches. From group theory calculations, for C_{2v} coordination sphere geometry, stretching modes of Cu—O(*R*COO) and Cu—P(dppe) should be of the A_1 and B_1, type and O—Cu—O and P—Cu—P deformation modes of the B_1 type (all IR active). Cu—O(*R*COO) bands were detected at 318 and 326 cm^{-1} (B_1), 243 and 248 cm^{-1} (A_1), for **1** and **3**, respectively. This is slightly higher than in the analogous Cu(I) carboxylate complexes with triphenyl phosphite, where bridging carboxylates were found [18]. Cu—P vibrations (A_1, B_1) were detected at 160 cm^{-1} and 132 cm^{-1} in accordance with results reported by others and in favour of the chelating coordination of dppe [2].

Acknowledgements

R. K. wishes to thank the Polish Committee for Scientific Research (KBN) for financial support *via* grant 3 T09A 118 18 and especially would like to thank Prof. Sven Harnung from Copenhagen University for his help with NMR measurements.

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