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Insertion reactions of organic anhydrides into the M–O bond of CuO^tBu and $Sb(OMe)_3$

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Abstract

The synthesis and structural characterization of the copper salts $[Cu_2(2\text{-Boc-benzoate})_4(dme)_2]$ (**1**), $[Cu(2\text{-Boc-benzoate})_2(tmeda)]$ (**2**), $[Cu_2(2\text{-Boc-benzoate})_2(dppm)]$ (**3**), $[Cu(2\text{-Boc-nicotinate})(PPh_3)_2]$ (**4**), $[Cu_2\{2\text{-Boc-5,6-anhydride-naphthylcarboxylate}\}_2(dppm)_2]$ (**5**) [dme = 1,2-dimethoxyethane, dppm = bis(diphenylphosphino)methane, tmeda = *N*,*N*′-tetramethylethylenediamine, Boc = *tert*-butoxycarbonyl] prove that cyclic organic anhydrides and dianhydrides readily insert into the Cu–O bond of $[CuO^tBu]$ forming carboxylate ligands with ester functionalities in the ligand periphery. $[Sb(CO_2Ph\text{-}o\text{-}CO_2Me)_2(OMe)(tmeda)]$ (**6**) was synthesised by insertion reaction of $Sb(OMe)_3$ with phthalic anhydride.

Keywords: Metal alkoxide; Organic anhydride; Insertion reactions

1. Introduction

Metal carboxylates have received a lot of attention due to their use in inorganic/organic hybrid materials and particularly metal oxalates have proven to be useful starting materials for the synthesis of ion-exchanging materials, molecular magnets and catalysts [1,2]. Copper carboxylates have also been used as catalysts for the decarboxylation of organic acids and several synthetic methods have been developed for the synthesis of copper(I) and copper(II) carboxylate complexes [3]. Syntheses of copper(I) and copper(II) carboxylates under aprotic conditions were achieved by the reaction of Cu(I) oxide and organic anhydrides as starting materials [4]. Having investigated the reactivity of copper(I) *tert*-butoxide with trimethylsilyl derivatives of the heavier group 15 elements, antimony and bismuth, we have recently started looking at insertion reactions of organic anhydrides into the Cu–O bond of $[CuO^tBu]$ [5–7]. These gave rise to a series of functionalised copper carboxylates and further results are reported here. This type of reaction, originally applied by Bergman and coworkers to probe the reactivity of metal–oxygen bonds in late transition metal alkoxides [8], can be extended to the main group metal alkoxide $Sb(OMe)_3$ and the first compound resulting from these efforts is reported here.

2. Experimental

General remarks. All operations were carried out in an atmosphere of purified Argon. Solvents were dried over sodium/benzophenone. Maleic anhydride was recrystallized from diethylether. Dppm and phthalic anhydrid were purchased from Aldrich. $[CuO^tBu]$ was prepared according to a published procedure [9].

1. To a solution of 137 mg (1 mmol) CuO^tBu in 10 mL THF was added a solution of 148 mg (1 mmol) isobenzofuran-1,3-dione (in the following phthalic

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anhydride) in 15 mL THF. The resulting yellow solution was refluxed for 1 h and gradually a colour change to blue-green was observed. A red precipitate of copper was filtered off, the solvent was changed to DME and 1 ml toluene was added. Storage of the solution at 4 °C for 2 days yielded blue crystals of **1**. Yield: 0.23 g (71.5%), m.p. 240 °C. *Anal.* Calc. for $C_{60}H_{82}Cu_2O_{22}$ (with one DME): C, 56.20; H, 6.45. Found: C, 56.38; H, 6.45%. UV/Vis (THF): $\lambda_{max}(\varepsilon)$ 669 nm (184); IR (CsJ, Nujol): $\tilde{\nu}/cm^{-1} = 1721$, 1627, 1596 ($COO^-$, C=O) cm^{-1}.

2. To a solution of 148 mg (1 mmol) phthalic anhydride in 5 mL DME was added a solution of 137 mg (1 mmol) [CuO^{t}Bu] in 10 mL DME and 0.15 mL (1 mmol) TMEDA. After addition of TMEDA the colour changes to dark green. A red precipitate of elemental copper was filtered off. After filtration the solvent was reduced to approximately 3 mL, and 1 mL hexane was added. Storage of the solution at 0 °C for two days produced blue crystals of **2**. Yield: 0.52 g, 83%; m.p. 214 °C. *Anal.* Calc. for $C_{30}H_{42}CuN_2O_8$: C, 57.91; H, 6.80; N, 4.50. Found: C, 57.60; H, 6.90; N, 4.50%. UV/Vis (thf): λ_{max} (ε) 677 nm (118); IR (CsI, Nujol) $\tilde{\nu} = 1721$, 1612, 1586, 1558 (COO^-, C=O) cm^{-1}.
3. To a solution of 148 (1 mmol) phthalic anhydride in 5 mL THF was added a solution of 137 mg (1 mmol) [CuO^{t}Bu] in 5 mL THF. The resulting yellow solution was stirred for 1 h at RT and gradually a colour change to blue-green was observed. After stirring, a solution of 193 mg (0.50 mmol) dppm in 5 mL THF was added. The resulting yellow solution was filtered and the solvent was reduced to approximately 5 mL and layered with 30 mL hexane. Storage of the solution at RT for one week produced colourless crystals of **3**. Yield: 0.41 g (86%); m.p. 220 °C. *Anal.* Calc. for $C_{49}H_{48}Cu_2O_8P_2$: C, 61.69; H, 5.07. Found: C, 61.62; H, 4.89%. IR (CsI, Nujol) $\tilde{\nu} = 1726$, 1607, 1588, 1565, 1582 (COO^-, C=O), 1484, 1436 (P–Ph) cm^{-1}; $^{31}P\{^1H\}$ NMR ([D_6]-DMSO, 25 °C, 161.975 MHz, 85%H_3PO_4): −6.6 (s); ^1H NMR ([D_6]-DMSO, 25 °C, 400 MHz, TMS): 7.8–6.9 (m, 26H, ar.), 3.2 (m, 2H, $Ph_2P\mathbf{CH_2}PPh_2$), 1.4 (s, 18 H, O^{t}Bu); $^{13}C\{H\}$ NMR ([D_6]-DMSO, 25 °C, 400 MHz, TMS) 173.62 (COO^-), 168.28 (COO^{t}Bu), 133.9–127.7 (C ar.), 81.3 (s, O–CMe_3), 28.1 (s, Me) ppm.
4. To a solution of 137 mg (1 mmol) [CuO^{t}Bu] in 10 mL THF was added a solution of 157 mg (1 mmol) pyridine-2,3-dicarboxylic anhydride in 5 mL THF. The resulting yellow solution with white precipitate was stirred for 1 h at RT and a solution of 524 mg (2 mmol) PPh_3 in 10 mL THF was added. The yellow solution was filtered, reduced to approximately 5 mL and layered with 30 mL hexane. Storage of the solution at RT for one week produced colorless crystals of **4**. Yield: 0.53 g (76%); m.p. 109 °C. *Anal.* Calc. for $C_{47}H_{42}CuNO_4P_2$: C, 69.66; H, 5.22; N, 1.73. Found: C, 69.47; H, 5.07; N, 1.89%. IR (CsI, Nujol) $\tilde{\nu} = 1716$, 1592 (COO^-, C=O), 1571, 1550 (C–N) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 161.975 MHz, 85%H_3PO_4): −2.28 (s, PPH_3); ^1H NMR ($CDCl_3$, 25 °C, 300 MHz, TMS): 8.6–7.24 (m, 33H, ar.), 3.8 (m, 4H, THF), 1.4 (s, 9H, O^{t}Bu); $^{13}C\{H\}$ NMR ($CDCl_3$, 25 °C, 400 MHz, TMS) 167.60 (COO^-), 138.29–128.69 (m, C. ar.), 27.95 (s, Me) ppm.
5. 268 mg (1 mmol) of 1,4,5,8-naphthalenetetracarboxylic dianhydride in 10 mL THF was suspended and a solution of 137 mg (1 mmol) [CuO^{t}Bu] was added. The reaction was heated and refluxing for 1 h created an orange coloured clear solution. After addition of 385 mg (1 mmol) dppm in 10 mL THF a colour change to yellow was observed. The solution was filtered, reduced to approximately 4 mL and 1 mL hexane was added. Storage at 4 °C produced yellow-orange crystals of **5**. Yield: 0.64 g (82%); m.p. 205 °C. *Anal.* Calc. for $C_{110}H_{118}Cu_2O_{20}P_4$ (with 5 THF): C, 65.69; H, 5.91. Found: C, 65.22; H, 5.93%; IR (KBr) $\tilde{\nu} = 1712$, 1593 (COO^-, C=O), 1434 (P–Ph_3);
6. To a solution of 215 mg (1 mmol) [$Sb(OMe)_3$] in 10 mL, 296 mg (2 mmol) phthalic anhydride in 5 mL THF was added. The resulting white precipitate was stirred for 1 h at RT. The precipitate was dissolved upon addition of 0.15 mL (1 mmol) TMEDA. After filtration the solution was reduced to approximately 3 mL and storage at 4 °C produced colourless crystals of **6**. Yield: 0.53 g (76%); m.p. 109 °C. *Anal.* Calc. for $C_{29}H_{41}$- $N_2O_{10}Sb$ (with one molecule of THF as lattice-bound solvent): C, 49.80; H, 5.91; N, 4.01. Found: C, 49.43; H, 5.95; N, 4.38%; IR (CsI, Nujol) $\tilde{\nu} = 1722$, 1643, 1570 (COO^-, C=O), 1373, 1332, 1294, 1256, 1112, 1076, 1029 (C–N) cm^{-1}.

2.1. X-ray crystallographic study

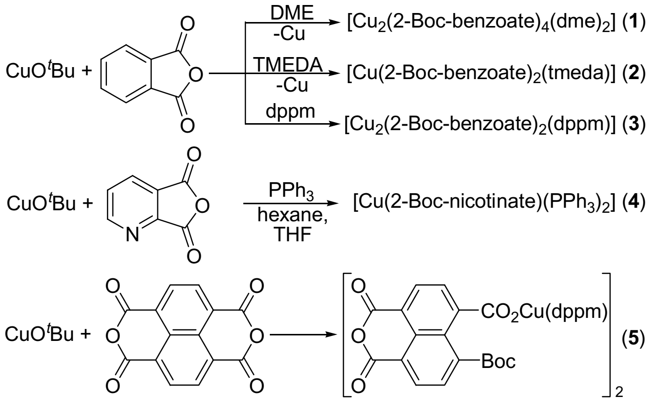
Data for **2** were collected on a STOE STADI 4 diffractometer equipped with a CCD detector. Data for **1**, **3–6** were collected on a STOE IPDS II diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the SHELXTL program package [10]. Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters. Disordered components (lattice-bound solvent) were assigned isotropic thermal parameters. Crystals of **3** were of poor quality and all C atoms were refined with isotropic thermal parameters. The crystallographic data and structure refinement parameters for the compounds are listed in Table 1.

3. Results and discussion

Reactions of phthalic anhydride with [CuO^{t}Bu] in a variety of donor solvents afforded compounds **1–4** (Scheme 1). At RT, insertion of the anhydride into the Cu–O bond of [CuO^{t}Bu] afforded in a disproportionation reaction **1**

Table 1
Details of the X-ray data collection and refinements

Compound	1	2	3	4	5	6
Formula	$C_{60}H_{82}Cu_2O_{22}$	$C_{30}H_{42}CuN_2O_8$	$C_{49}H_{48}Cu_2O_8P_2$	$C_{47}H_{42}CuNO_4P_2$	$C_{102}H_{102}Cu_2O_{18}P_4$	$C_{29}H_{41}N_2O_{10}Sb$
Formula weight	1282.35	622.20	953.89	810.30	1866.80	699.39
T (K)	200(2)	200(2)	100(2)	110(2)	120(2)	200(2)
Crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a (Å)	11.2269(9)	9.058(1)	12.194(2)	10.386(2)	18.855(4)	14.199(2)
b (Å)	12.896(1)	12.592(2)	21.224(4)	13.422(3)	23.594(5)	26.279(5)
c (Å)	12.998(1)	14.247(2)	17.133(3)	14.809(6)	24.410(5)	8.522(3)
α (°)	108.073(9)	94.90(1)	90	96.50(2)	90	90
β (°)	108.358(8)	97.45(1)	92.14(4)	101.62(2)	107.42(3)	96.69(3)
γ (°)	104.574(8)	96.45(1)	90	97.12(2)	90	90
V (Å^3)	1565.6(3)	1593.3(4)	4431.0(15)	1985.9(9)	10361(4)	3157.9(14)
Z	1	2	4	2	4	4
ρ_{calc} (Mg m^{-3})	1.360	1.297	1.430	1.335	1.197	1.471
F(000)	676	658	1976	844	3904	1440
μ (mm^{-1})	0.755	0.734	1.086	0.676	0.534	0.930
θ-range (°)	3.89–31.91	3.71–31.91	2.26–25.00	1.54–27.05	1.23–26.08	2.12–25.89
Reflections collected	8290	11149	5709	4281	26175	15104
Unique date	6343	6944	4644	4015	15106	5883
$R_{int.}$	0.0284	0.0857	0.1078	0.0411	0.0889	0.0412
Parameters	387	380	233	496	1036	386
wR_2 (all data)	0.0869	0.2101	0.1322	0.1474	0.1486	0.0825
S (Goodness-of-fit)	0.894	0.908	0.923	0.879	0.925	1.042
R_1 [$I > 2\sigma(I)$]	0.0425	0.0721	0.0938	0.0570	0.0705	0.0320
Peak, hole (e Å^{-3})	0.503, −0.395	0.573, −1.027	0.431, −0.382	0.417, −0.386	0.386, −0.348	0.547, −0.749



Scheme 1. Synthesis of **1**–**5** (dme = 1,2-dimethoxyethane; tmeda = *N*,*N*′-tetramethylethylenediamine; dppm = bis(diphenylphosphino)methane, py = C_5H_3N, Boc = *tert*-butoxycarbonyl).

together with elemental copper. The formation of **1** proceeds slowly overnight when carried out at RT and phthalic anhydride is transformed into the 2-Boc-benzoate anion.

The solid-state structure of **1** consists of dicopper(II) tetracarboxylate 'paddlewheel' units (Fig. 1). The coordination geometry and bonding parameters of the copper atoms found in **1** are common for Cu(II) carboxylates and a wealth of structural and theoretical accounts for these systems exist [3].

When the reaction was performed in the presence of TMEDA, **2** was obtained (Scheme 1). Insertion of phthalic anhydride into the Cu–O bond occurred and tmeda acts as a chelating ligand for the Cu(II) centre in **2** unlike dme in the solid-state structure of **1** (Fig. 2).

The Cu atom in **2** is bonded to a bidentate tmeda ligand [Cu–N 2.015(4) and 2.025(4) Å] and two 2-Boc-benzoato ligands. The carboxylate groups are essentially monodentate with Cu–O distances of 1.975(3) and 1.972(3) Å (Fig. 2). The oxygen atoms O(2) and O(6) [Cu–O ca. 2.4 Å] complete the distorted octahedral coordination sphere of Cu(1) in **2**. Similar Cu–O bond distances and angles around the Cu(II) centre were observed in [Cu(fum)(tmeda)] · $2H_2O$ (fum = fumarate) and in an isostructural 2-Boc-maleato complex [6,7]. In the presence of tertiary phosphines disproportionation can be suppressed, e.g., in the presence of dppm, **3** was obtained (Fig. 3, Scheme 1).

In the solid-state, **3** consists of two three-coordinated Cu(I) centres held together by two 2-Boc-benzoato and one dppm ligand. Cu(1) and Cu(2) are each coordinated by a P atom of a dppm ligand [Cu–P 2.166(4) and 2.164(4) Å] and two oxygen atoms of two 2-Boc-benzoato ligands. A similar reaction with maleic anhydride, produced one dimeric complex with central Cu_2O_2 four-membered ring [6]. Here, however, formation of larger aggregates might be hindered by the steric requirements of the generated ligands. By changing the nature of anhydrides involved in insertion reactions, the synthesis of larger aggregates is a possibility. Therefore, a number of pyridyl-containing organic anhydrides were investigated and it was hoped that additional N-donor centres will form extended coordination oligomers or polymers. So far, however, this has either resulted in insoluble and amorphous

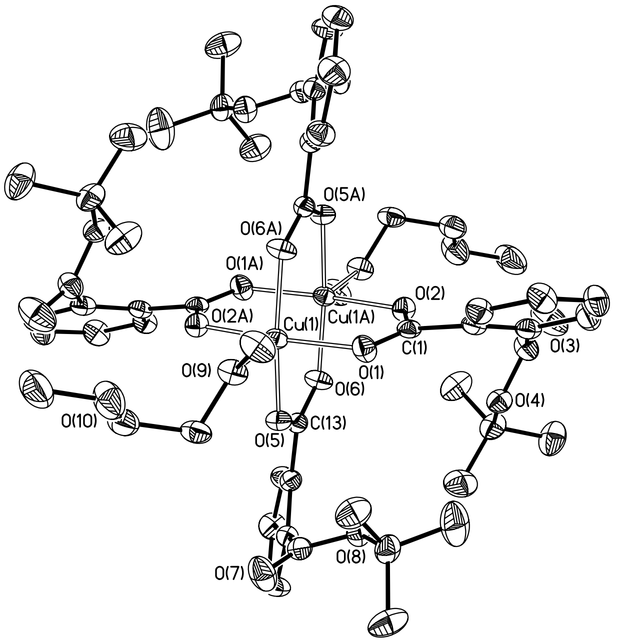


Fig. 1. Molecular structure of **1** in the solid state (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Final label A denotes symmetry operations: $-x+1$, $-y+2$, $-z+1$ and $-x$, $-y+1$, $-z+1$. Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.9519(19), Cu(1)–O(5) 1.9540(18), Cu(1)–O(6A), 1.9573(18), Cu(1)–O(2A) 1.9599(18), Cu(1)–O(9) 2.1874(17), O(1)–Cu(1)–O(5) 90.19(8), O(1)–Cu(1)–O(6A) 87.93(8), O(5)–Cu(1)–O(6A) 169.80(7), O(1)–Cu(1)–O(2A) 169.76(7), O(5)–Cu(1)–O(2A) 88.12(8), O(6A)–Cu(1)–O(2A) 91.96(8), O(1)–Cu(1)–O(9) 95.18(7), O(5)–Cu(1)–O(9) 95.72(7), O(6A)–Cu(1)–O(9) 94.43(7), O(2A)–Cu(1)–O(9) 95.04(7).

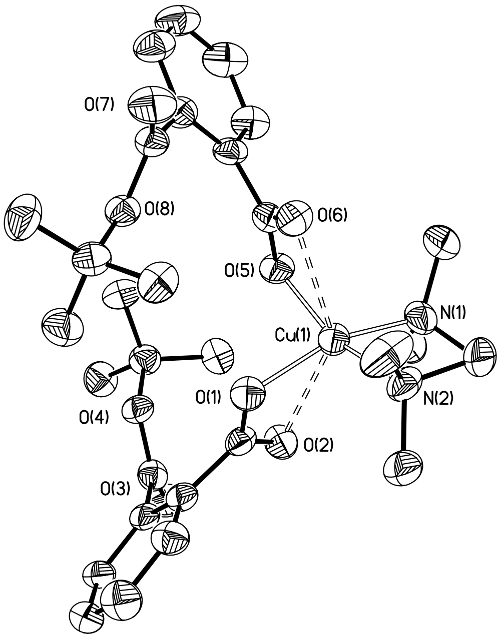


Fig. 2. Molecular structure of **2** in the solid state (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.975(3), Cu(1)–O(5) 1.972(3), Cu(1)–N(1) 2.015(4), Cu(1)–N(2) 2.025(4), O(5)–Cu(1)–O(1) 95.61(14), O(5)–Cu(1)–N(1) 91.77(16), O(1)–Cu(1)–N(1) 160.19(14), O(5)–Cu(1)–N(2) 159.77(14), O(1)–Cu(1)–N(2) 91.88(16), N(1)–Cu(1)–N(2) 87.36(18).

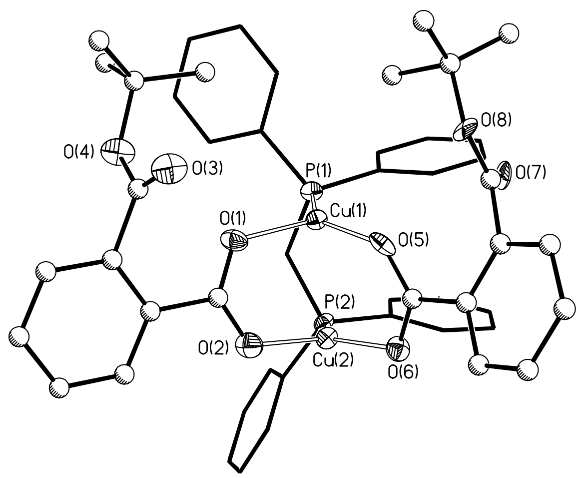


Fig. 3. Molecular structure of **3** in the solid state (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 2.015(12), Cu(1)–O(5) 1.958(10), Cu(1)–P(1) 2.166(4), Cu(2)–O(2) 1.996(13), Cu(2)–O(6) 2.003(10), Cu(2)–P(2) 2.164(4), O(5)–Cu(1)–O(1) 101.8(4), O(5)–Cu(1)–P(1) 138.9(3), O(1)–Cu(1)–P(1) 118.9(3), O(2)–Cu(2)–O(6) 102.3(4), O(2)–Cu(2)–P(2) 123.3(3), O(6)–Cu(2)–P(2) 134.4(4).

compounds or as is demonstrated by the reaction of a solution of [CuO^{t}Bu] with pyridine-2,3-dicarboxylic anhydride in the presence of the PPh_3 has resulted in mononuclear complexes like **4** (Scheme 1). The solid-state structure of **4** consists of a distorted-tetrahedrally surrounded Cu atom (Fig. 4). The generated carboxylate group chelates Cu(1), with Cu–O distances of 2.172(6) and 2.280(8) Å. The tetrahedral coordination sphere is completed by two P atoms of two PPh_3.

Surprisingly, out of the two potential products (2-Boc-nicotinato- or 3-Boc-picolinato-anions could be formed in the course of the reaction) the Cu salt of 2-Boc-nicotinic acid was formed, a fact which could be rationalised by nitrogen pre-coordination of [CuO^{t}Bu] and ester formation with the closest carbonyl group.

Previously, it was shown that insertion reactions of organic dianhydrides and [CuO^{t}Bu] result in Cu(I) complexes if the reactions are either kept at low temperature or performed in the presence of phosphine donors [6,7]. The stepwise opening, however, has not yet been achieved. In a reaction of [CuO^{t}Bu] with the anhydride of naphthalene-1,4,5,8-tertcarboxylic acid in the ratio 1:1, the phosphine-stabilized copper salt of **5** was obtained. Solid samples of **5**, are insoluble once isolated but the molecular structure of **5** could be confirmed by X-ray crystallography (Fig. 5).

Compound **5** consists of one [Cu_2(dppm)$_2$] unit [Cu(1)···Cu(2) 2.980(2) and Cu–P av. 2.24 Å]. Each copper atom is coordinated by one oxygen atom O(1), O(8) of the monodentate carboxylate group in the generated carboxylato ligand, resulting in a distorted trigonal planar coordination environment for Cu(1) and Cu(2). Examples for three-coordinated Cu atom in Cu(I) dicarboxylates are found in Cu(I) perfluorosuccinate, copper(I) glutarate and in the ion-separated complex [Cu(OAc)(BF_4)(dppm)$_2$]

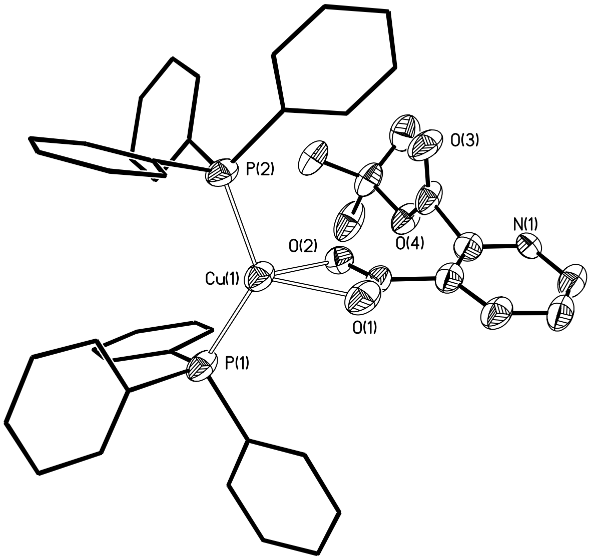


Fig. 4. Molecular structure of **4** in the solid state (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 2.172(6), Cu(1)–P(1) 2.234(3), Cu(1)–P(2) 2.250(2), Cu(1)–O(2) 2.280(8), O(1)–Cu(1)–P(1) 113.3(2), O(1)–Cu(1)–P(2) 116.6(2), P(1)–Cu(1)–P(2) 128.73(10), O(1)–Cu(1)–O(2) 59.8(3), P(1)–Cu(1)–O(2) 111.09(19), P(2)–Cu(1)–O(2) 103.3(2).

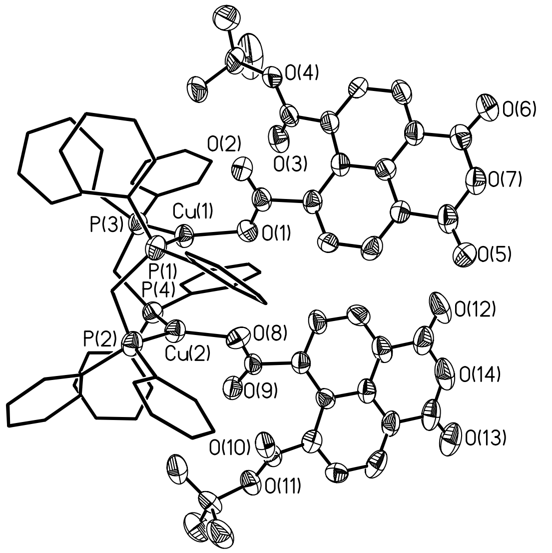
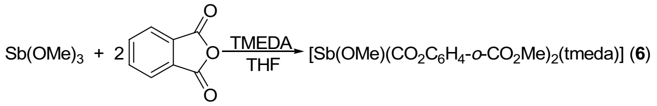


Fig. 5. Molecular structure of **5** in the solid state (ellipsoids at 50% probability level; hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Cu(1)–O(1) 1.973(5), Cu(1)–P(3) 2.2305(18), Cu(1)–P(1) 2.256(2), Cu(2)–O(8) 1.991(5), Cu(2)–P(2) 2.230(3), Cu(2)–P(4) 2.2449(19), O(1)–Cu(1)–P(3) 127.77(15), O(1)–Cu(1)–P(1) 115.01(16), P(3)–Cu(1)–P(1) 116.61(8), O(8)–Cu(2)–P(2) 115.56(17), O(8)–Cu(2)–P(4) 118.58(18), P(2)–Cu(2)–P(4) 125.86(8).

[3b,11,12]. The investigation of stepwise opening reactions of polyanhydrides is ongoing and further results are to be expected.



Scheme 2. Synthesis of **6** (tmeda = *N*,*N*′-tetramethylethylenediamine).

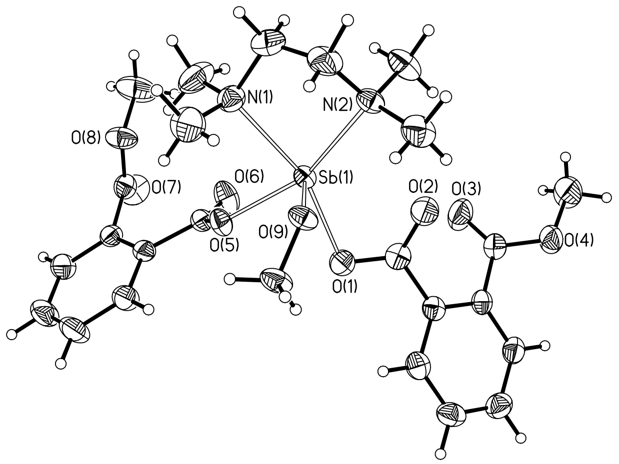


Fig. 6. Molecular structure of **6** in the solid state (ellipsoids at 50% probability level). Selected bond lengths (Å) and angles (°): Sb(1)–O(1) 2.235(2), Sb(1)–O(5) 2.132(2), Sb(1)–O(9) 1.951(2), Sb(1)–N(1) 2.490(3), Sb(1)–N(2) 2.595(3), O(9)–Sb(1)–O(5) 84.67(8), O(9)–Sb(1)–O(1) 86.38(9), O(5)–Sb(1)–O(1) 82.48(9), O(9)–Sb(1)–N(1) 85.69(9), O(5)–Sb(1)–N(1) 79.94(9), O(1)–Sb(1)–N(1) 161.30(9), O(9)–Sb(1)–N(2) 75.75(8), O(5)–Sb(1)–N(2) 146.62(9), O(1)–Sb(1)–N(2) 122.14(9), N(1)–Sb(1)–N(2) 71.96(9).

Finally, a first result from efforts to apply insertion reactions of organic anhydrides into the metal–O bond of metal alkoxides in main group metal alkoxide chemistry is described. As a model compound $Sb(OMe)_3$ was reacted with phthalic anhydride giving rise to **6** in which one methoxy group is retained (Scheme 2, Fig. 6).

Crystals of **6** could only be obtained in the presence of the additional donor TMEDA and in the solid state, **6** consists of a pentacoordinated Sb centre in distorted square-pyramidal coordination environment. The central antimony atom is surrounded by a chelating TMEDA ligand and two monodentate 2-Boc-benzoato ligands, whilst the remaining methoxy group forms the top of the square-pyramidal arrangement.

4. Conclusion

The syntheses and structural characterisation of the copper carboxylates **1**–**5** prove that cyclic organic anhydrides readily insert into the Cu–O bond of [CuO^{t}Bu] forming carboxylate ligands with ester functionalities in the ligand periphery. These donor centres may be used in the construction of complex aggregates with different dimensionality either by stabilising other metal centres or suitable organics, e.g., polyols, amines, etc. The experience gathered in this area so far, however, indicates that possibly new synthetic approaches are necessary to overcome solubility problems. The incorporation of main group metals via the anhydride/metal alkoxide route (here antimony) represents a new development in this area and more examples of novel complexes can be expected.

5. Supplementary material

CCDC 641382, 641383, 641384, 641385, 641386 and 641387 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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