Copper(II) complexes bearing cyclobutanecarboxylate and pyridine ligands: a new series of dinuclear paddle-wheel complexes

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Abstract

Four members of a new series of paddle-wheel copper(II) complexes bearing cyclobutanecarboxylate as bridging ligand with pyridine derived ligands in axial positions are reported. They have been characterised by FTIR-ATR, UV–Vis spectroscopy, mass spectrometry, and single crystal X-ray diffraction. The synthesis is straight-forward by combining the carboxylic acid, copper(II) acetate, and a slight excess of a pyridine ligand. The molecular structures of three complexes reveal a coordination mode expected for such type of dinuclear copper(II) carboxylates.

Graphic abstract

Keywords Copper(II) complexes · Paddle-wheel structure · Crystal structure

Introduction

The combination of copper(II) salts with aromatic or alkyl carboxylic acids $R\text{--COOH}$ often yield binuclear paddle-wheel complexes [1–3]. The vacant axial position can be occupied by various ligands L , whereas pyridines and its derivatives are most frequently used [4–7]. Due to the

robustness and reliability of the preparation with numerous combinations of R and L (see Scheme 1) and due to advantageous coordination geometry in axial direction, such paddle-wheel structures have been used for the synthesis of MOFs, coordination polymers, and related materials [8–10].

Interestingly, cycloalkane carboxylates are extremely rarely used for binuclear copper complexes [11–13] and no crystal structures of such complexes have been determined so far. In this work we present paddle-wheel type copper(II) complexes bearing cyclobutanecarboxylate as bridging ligand, which is a carboxylic acid generally not frequently used in coordination chemistry. Pyridine derived ligands are used as axial ligands. The complexes were characterised by FTIR-ATR and UV–Vis spectroscopy as well as by single crystal X-ray diffraction.

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Scheme 1

Results and discussion

Synthesis and characterisation

The complexes **1–4** were prepared by combining copper(II) acetate, an excess of the pyridine ligand, and cyclobutane-carboxylic acid in methanolic solutions at room temperature under aerobic conditions (Scheme 2). Upon stirring, the complexes precipitated out of solution as intense green powders. Crystals of all complexes could be obtained by re-crystallisation from methanol and are stable under ambient conditions.

The compounds were characterised by FTIR-ATR, UV–Vis spectroscopy and mass spectrometry. The FTIR-ATR spectra are shown in the supplementary material (Fig. S1). For the methyl-nicotinate ligands (**3** and **4**), a signal can be found at 1731 cm^{-1} , which is characteristic for the $-\text{COOMe}$ group and thus is absent for **1** and **2**. For the bridging carboxylate, characteristic symmetric and asymmetric vibrations, $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$, can be found at $\sim 1607\text{ cm}^{-1}$ and $\sim 1421\text{ cm}^{-1}$, respectively. The difference between these bands is 186 cm^{-1} which is indicative of a bridging binding mode of the carboxylate ligands [2, 10, 14].

In the positive mode ESI mass spectra no signals can be found for the intact complexes. However, for each compound several fragment-peaks could be identified, e.g., $[\text{Cu}_2(\text{BuCOO})_3(\text{s-py})_x]^+$ ($x = 1, 2$) (Figs. S2–S5).

In the UV–Vis spectra, each complex features a broad absorption at around 700 nm with a low extinction coefficient of around $150\text{ mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$ which is characteristic of d–d transitions [10, 15]. For **1** and **2**, π – π^* transitions

Fig. 1 UV–Vis absorption spectrum of **1** in methanol

Table 1 UV–Vis spectroscopic data of the complexes **1–4**

Substance	λ/nm ($\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$)
1	256 (8950), 706 (158)
2	255 (8703), 706 (142)
3	217 (22,552), 261 (10,272), 699 (145)
4	212 (20,334), 271 (8370), 700 (141)

of the pyridine moieties are found at $\sim 255\text{ nm}$ (Figs. 1, S6) [16, 17]. For **3** and **4**, these absorptions are shifted to 261 – 271 nm with additional short wavelength bands at 212 – 217 nm (Figs. S7, S8) (Table 1).

Structural studies

All complexes were obtained as crystalline solids suitable for single crystal X-ray analysis by slow evaporation of their methanolic solutions. However, only the structures of **1**, **3**, and **4** could be solved. For **2**, a unit cell of high symmetry (presumably tetragonal or orthorhombic) could be determined but no reliable structure solution could be found in numerous space groups maybe due to twinning of

Scheme 2

Fig. 2 Molecular structures of **1**, **3**, and **4**. Displacement ellipsoids were drawn at 50% probability level. Hydrogen atoms are omitted for clarity

the crystals.¹ The molecular structures of **1**, **3**, and **4** are depicted in Fig. 2 and selected bond lengths and bond angles are summarized in Table 2. Detailed crystallographic data are presented in Table 3. Complexes **1** and **3** were found to crystallise in the monoclinic space groups $P2_1/n$ and $C2/c$, respectively. Complex **4** crystallises in the triclinic space group $P\bar{1}$. For **1** and **4** the asymmetric unit consist of one, for **3** it consists of a half formula unit. In all complexes, four carboxylates bridge two copper atoms forming a paddle-wheel like structure. In the axial positions the pyridine ligands are completing the coordination environment. Only **3** has a crystallographic imposed symmetry with an inversion centre bisecting the Cu–Cu bond. However, the other two complexes show a very similar geometry with just small deviation from inversion symmetry. With 1.954–1.999 Å (Cu–O) and 2.166–2.195 Å (Cu–N) the bond lengths are in the expected region. The pyridine ligands are both coplanar to each other. Interestingly, the pyridine plane is not bisecting the O–Cu–O angle which would be expected based

Table 2 Selected bond lengths/Å and bond angles/° for **1**, **3**, and **4**

	1	3	4
Cu1–O	1.951(3)	1.972(2)	1.961(3)
	1.972(2)	1.972(2)	1.965(3)
	1.982(2)	1.976(2)	1.971(3)
	1.986(2)	1.981(2)	1.976(3)
Cu2–O	1.954(2)		1.954(3)
	1.956(2)		1.967(3)
	1.990(2)		1.968(3)
	1.999(2)		1.968(3)
Cu1–N1	2.166(3)	2.186(2)	2.194(3)
Cu2–N2	2.171(3)		2.195(3)
Cu–Cu	2.6324(6)	2.6176(6)	2.6156(7)

on steric considerations but have a small dihedral angle O–Cu–N–C with values between 26–42° for **1** and 14–30° for **3** and **4**. The cyclobutane moiety is somewhat flexible as indicated by comparable high thermal ellipsoids of some of its carbon atoms.

¹ At room temperature, a unit cell with following parameters could be determined: 14.757 Å, 21.791 Å, 21.819 Å, 90.00°, 89.99°, 90.01°. At low temperature, the crystals lose crystallinity.

Table 3 Crystal data for the structures of **1**, **3**, and **4**

Compound	1	3	4
Empirical formula	C ₃₀ H ₃₈ Cu ₂ N ₂ O ₈	C ₁₇ H ₂₁ CuNO ₆	C ₃₄ H ₄₂ Cu ₂ N ₂ O ₁₂
Formula weight	681.70	398.89	797.77
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
Temp/K	150	100	100
<i>a</i> /Å	10.347(1)	19.430(2)	12.197(1)
<i>b</i> /Å	17.091(2)	19.616(2)	12.661(1)
<i>c</i> /Å	17.314(2)	9.784(1)	13.107(1)
α /°	90	90	72.456(1)
β /°	96.377(1)	114.174(2)	75.421(1)
γ /°	90	90	66.941(1)
<i>V</i> /Å ³	3042.9(6)	3402.1(6)	1755.0(3)
<i>Z</i>	4	8	2
<i>D</i> _{calc} /g cm ^{−3}	1.488	1.558	1.510
Reflns collected	24,442	19,608	15,974
Indep. reflns	4452	3360	5114
Obs. reflns [<i>I</i> > 2σ(<i>I</i>)]	3505	2773	3632
Param. refin./ restr	379/0	227/0	455/0
Absorption correction	Multi-scan	Multi-scan	Multi-scan
<i>R</i> ₁	0.037	0.037	0.041
<i>wR</i> ₂	0.099	0.103	0.114
CCDC	1981162	1981163	1981164

Conclusion

In conclusion, we have presented four members of a new series of paddle-wheel complexes bearing cyclobutanecarboxylate as bridging ligand. The synthesis is straight-forward with the combination of the carboxylic acid, copper(II) acetate, and a slight excess of the pyridine ligand. Although crystals could be obtained for all complexes, the crystal structure of only three complexes could be determined by single-crystal X-ray diffraction. All attempts to solve the structure of the 4-ethylpyridine derivative failed so far. The other complexes reveal the coordination mode expected for such type of binuclear copper(II) carboxylates.

Experimental

All solvents and reagents were commercially available and used as received. FTIR-ATR spectra were recorded on a Bruker Tensor 27 FT-IR with ATR unit. The spectra were recorded directly from dry powder of each complex.

HR-MS measurements were carried out on an Agilent 6520 QTOF mass spectrometer with an ESI source. For photophysical characterization, spectroscopic grade solvents were used throughout all measurements. Absorption spectra were recorded with a Cary 100 Bio UV–Vis spectrophotometer.

General procedure for the synthesis of complexes 1–4

The pyridine-type ligand (1.9 mmol; pyridine: 150 mg, 4-ethylpyridine: 204 mg, methyl-nicotinate/methyl-isonicotinate: 260 mg) and 96 mg of the carboxylic acid (0.96 mmol) are dissolved in 10 cm³ MeOH. Copper(II) acetate monohydrate (96 mg, 0.48 mmol) is dissolved in 20 cm³ methanol. Both solutions are mixed while stirring. The solution appears to be blue-green. Methanol is evaporated at room temperature until the complex precipitates. The complex is separated from the solvent by filtration over a Büchner-funnel and is washed with 10 cm³ of cold MeOH. The compound is dried at room temperature under ambient condition. All compounds are green.

Tetrakis(μ-cyclobutanecarboxylato)-bis(pyridine)-di-copper(II) (1, C₃₀H₃₈Cu₂N₂O₈) Yield 0.05 g (31%); ESI-MS: *m/z* (calc.): [Cu₂(^cBuCOO)₃py₂]⁺ 581.077 (581.077), [Cu₂(^cBuCOO)₃py]⁺ 502.035 (502.035), [Cu₂(^cBuCOO)₃(MeO) + Na]⁺ 477.001 (477.001); FT-IR (ATR): $\bar{\nu}$ = 1011w, 1036m, 1074w, 1109w, 1151w, 1219m, 1248w, 1298s, 1422s, 1447m, 1599s, 1607s, 2866w, 2939w, 2980w cm^{−1}.

Tetrakis(μ-cyclobutanecarboxylato)-bis(4-ethylpyridine)-di-copper(II) (2, C₃₄H₄₆Cu₂N₂O₈) Yield 0.07 g (43%); ESI-MS: *m/z* (calc.): [Cu₂(^cBuCOO)₃EtPy₂]⁺ 637.139 (637.117), [Cu₂(^cBuCOO)₃EtPy]⁺ 530.048 (530.066), [Cu₂(^cBuCOO)₃EtPy₂]⁺ 376.108 (376.121); FT-IR (ATR): $\bar{\nu}$ = 1020m, 1053w, 1070w, 1097w, 1223m, 1242m, 1296s, 1422s, 1607s, 2866w, 2938w, 2966w, 2983sh cm^{−1}.

Tetrakis(μ-cyclobutanecarboxylato)-bis(methylisonicotinate)-di-copper(II) (3, C₃₀H₃₈Cu₂N₂O₈) Yield 0.11 g (57%); ESI-MS: *m/z* (calc.): [Cu₂(^cBuCOO)₃(4-MeOOCpy)₂]⁺ 697.094 (697.088), [Cu₂(^cBuCOO)₃(4-MeOOCpy)]⁺ 560.047 (560.040), [Cu₂(^cBuCOO)(4-MeOOCpy)₂]⁺ 530.072 (530.017); FT-IR (ATR): $\bar{\nu}$ = 864m, 955m, 1018m, 1053w, 1063w, 1109w, 1123m, 1215w, 1229w, 1281ah, 1290s, 1327w, 1420s, 1435sh, 1562w, 1607s, 1732s, 2868w, 2945w, 2986w cm^{−1}.

Tetrakis(μ-cyclobutanecarboxylato)-bis(methylnicotinate)-di-copper(II) (4, C₃₄H₄₂Cu₂N₂O₁₂) Yield 0.14 g (73%); ESI-MS: *m/z* (calc.): [Cu₂(^cBuCOO)₃(3-MeOOCpy)₂]⁺ 697.080

(697.088), $[\text{Cu}_2(^c\text{BuCOO})_3(3\text{-MeOOCpy})]^+$ 560.035 (560.040), $[\text{Cu}_2(^c\text{BuCOO})(3\text{-MeOOCpy})_2]^+$ 530.061 (530.061); FT-IR (ATR): $\bar{\nu}$ = 1030m, 1047m, 1096m, 1117s, 1136m, 1194m, 1246s, 1285s, 1302sh, 1323w, 1422s, 1597s, 1607s, 1732s, 2870w, 2945w, 2982w cm^{-1} .

X-ray structure determination of complexes 1, 3, and 4

Suitable single crystals for X-ray diffraction were obtained for **1**, **3**, and **4** under ambient conditions from a methanolic solution of the respective compounds over a period of several days. Diffraction data were collected on a Bruker Smart Apex diffractometer operating with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods (SHELXL-2014/7) and refined by full-matrix least squares on F^2 (SHELXL-2014/7) [18]. The H atoms were calculated geometrically, and a riding model was applied in the refinement process. These data were deposited with CCDC with the following numbers: CCDC 1981162–1981164 and can be obtained free of charge from the Cambridge Crystallographic Data Centre at <https://summary.ccdc.cam.ac.uk/structure-summary-form>. Crystal data are given in Table 3.

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