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Synthesis of Metal Paddlanes: X-ray Structure Determination of Bis-(methyl nicotinate)copper(II) Acetate Dimer

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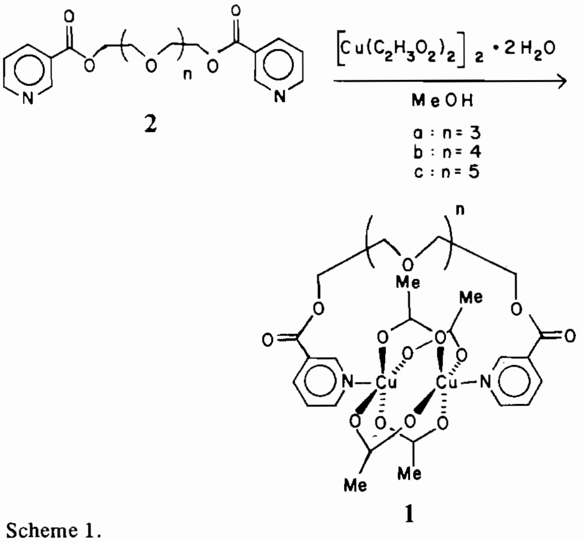
Abstract

The synthesis of nicotinic acid based *N,N'*-bidentate ligands capable of spanning the axial sites of copper(II) acetate dimer are reported. Reaction of these ligands with $[Cu(C_2H_3O_2)_2]_2 \cdot 2H_2O$ gave the 1:1 adduct: a metal paddlane, which on recrystallization from MeOH/CHCl$_3$ yielded the trans-esterified complex $[Cu(C_2H_3O_2)_2]_2 \cdot 2C_7H_7NO_2$, **3**. A single crystal X-ray structure determination of **3** is presented.

Introduction

Several attempts have been made to correlate the structural and magnetic properties in dinuclear metal(II) carboxylate complexes [1–5]. In order to further elucidate the interactions in these species we designed flexible *N,N'*-bidentate ligands and attempted construction of macrocyclic copper(II) carboxylate complexes (paddlanes) of the type **1** depicted in Scheme 1.



Scheme 1.

In the 1:1 complex of **2** with dimeric copper(II) acetate to form the metal paddlane **1**, variation of the chain length in the ligand (*n* = 3–5), was expected to systematically alter the copper acetate moiety and provide a better insight into the Cu–Cu interaction.

Reaction of nicotinoyl chloride [6] with an appropriate glycol in benzene gave **2** (*ca.* 100%), as colorless oils[†] ^{1}H NMR (CDCl$_3$) δ 7.42 (dd, 5-py$H$, $J_{5,6}$ = 4.9, $J_{5,4}$ = 7.9 Hz, 2H), 8.33 (ddd, 4-py$H$, $J_{4,2}$ = $J_{4,6}$ = 2.0, $J_{4,5}$ = 7.9 Hz, 2H), 8.78 (dd, 6-py$H$, $J_{4,6}$ = 2.0, $J_{5,6}$ = 4.9 Hz, 2H), 9.24 (d, 2-py$H$, J = 2.0 Hz, 2H)[§]. An equimolar mixture of **2** and $[Cu(C_2H_3O_2)_2]_2 \cdot 2H_2O$ in MeOH at 25 °C under high-dilution conditions [8, 9] yielded a bluish-green solid (**1**) *n* = 4: melting point 164–165 °C; *n* = 5: melting point 118–119 °C[†].

Although the complexation reaction which leads to **1** was conducted in MeOH, the only crystals obtained from the recrystallization of **1b** (*n* = 4) in MeOH/CHCl$_3$ was the methyl nicotinate complex of copper acetate **3** [melting point >225 °C (dec)] (Scheme 2)! The formation of **3** occurred by facile transesterification of the ligand portion of complex **1b** during recrystallization; recrystallizations from aprotic solvents do not give **3**. The fact that transesterification does not occur in the reaction is due to the relatively short reaction time (3 h) compared to recrystallization (1 week). In light of this the role of chloroform is simply that of a co-crystallization solvent. In addition, the commutation appeared to occur solely on the complexed ligand since attempted transesterifications of non-ligating esters (*i.e.*, benzoate esters) in the presence of copper acetate failed. Because of the mild reaction conditions (25 °C, MeOH/CHCl$_3$), participation by copper is not unlikely; however, this possibility has not been pursued. Slow evaporation of a MeOH/CHCl$_3$ solution gave single crystals of **3**. Due to the small

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[†] Satisfactory spectral and analytical data were obtained for each new compound.

[§] The proton NMR spectra of the polyether moiety in ligands **2a–c** had a standard pattern [7].

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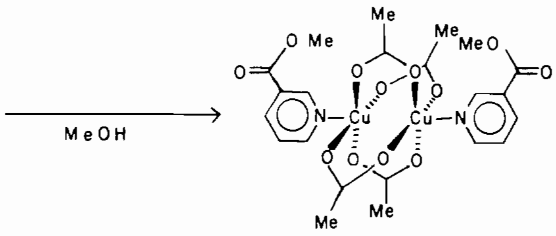
amount of material used in the recrystallization (~5 mg), no other products were isolated, nor was the yield determined.

1



3

Scheme 2.

Crystal Data

$Cu_2C_{22}H_{26}N_2O_{12}$, Formula weight = 637.5, monoclinic, space group $P2_1/c$, $a = 8.710(2)$, $b = 18.823(5)$, $c = 8.059(2)$ Å, $\beta = 92.56(2)°$, $Z = 2$, $D_c = 1.604$ g cm^{-3}, $T = 24$ °C, μ(Mo Kα) = 16.77 cm^{-1}, $R = 0.043$ for 1612 observed data.

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator, using a crystal of dimensions 0.14 × 0.32 × 0.42 mm. All data in one quadrant having $1° < \theta < 25°$ were measured by ω–2θ scans of variable rate. Scan rates varied 0.74–10.00 deg min^{-1} in order to measure all significant reflections with $I \simeq 50\sigma(I)$. Data reduction included corrections for background, decay (23%), Lorentz, and polarization effects, as well as absorption corrections based on ψ scans of reflections near $\chi = 90°$. The minimum relative transmission coefficient was 0.582. A total of 2328 unique data was measured, of which 1612 had $I > 3\sigma(I)$ and were used in the refinement.

The structure was solved by heavy atom methods and refined by full matrix least squares based on F with weights $w = \sigma^{-2}(F_o)$, using the Enraf-Nonius SDP programs [10]. Nonhydrogen atoms were treated anisotropically; hydrogen atoms were located by difference maps and included as fixed contributions. The maximum residual density in a final difference map was 0.72 eÅ^{-3}, near Cu.

Discussion

Fractional coordinates are given in Table I and selected bond distances are listed in Table II. The copper acetate dimer structure is observed with methyl nicotinate capping the apical positions. There is a center of symmetry between the two copper atoms. The Cu–Cu distance is 2.607(1) Å, which falls within the range of that observed in copper acetate complexes with *N*-donor ligands (2.58–2.67 Å) [3]. As well, the Cu–N distance of 2.173(3) Å is also within the normally observed range (2.08–2.24 Å) [3]. The geometry around copper is distorted tetragonal-pyramidal with the copper atom out of the basal plane of the four oxygens, displaced toward the nitrogen atom, by 0.197(1) Å as compared to similar compounds with a range of 0.19–0.23 Å [3]. The Cu–O distances average 1.974 Å. In both independent acetate groups, the two C–O distances differ by statistically significant amounts. Since no reason for this difference is readily apparent,

TABLE I. Coordinates for $Cu_2(C_2H_3O_2)_4(C_7H_7NO_2)_2$[a]

Atom	x	y	z
Cu	0.03823(6)	0.43308(3)	0.49606(6)
O1	−0.0601(4)	0.4297(1)	0.7124(4)
O2	0.1219(4)	0.4563(2)	0.2788(4)
O3	−0.1677(4)	0.4177(2)	0.3882(4)
O4	0.2312(4)	0.4685(2)	0.6011(4)
O5	0.4642(6)	0.1409(2)	0.3971(7)
O6	0.5004(5)	0.2518(2)	0.3115(6)
N1	0.1047(4)	0.3218(2)	0.5008(5)
C1	−0.1222(5)	0.4828(2)	0.7771(5)
C2	−0.2021(6)	0.4696(3)	0.9344(6)
C3	−0.2612(5)	0.4690(3)	0.3670(5)
C4	−0.4198(6)	0.4522(3)	0.2991(7)
C5	0.2341(5)	0.2978(3)	0.4448(6)
C6	0.2726(6)	0.2261(3)	0.4440(7)
C7	0.1721(7)	0.1785(3)	0.5085(8)
C8	0.0381(7)	0.2028(3)	0.5689(8)
C9	0.0087(6)	0.2744(3)	0.5652(7)
C10	0.4213(7)	0.2003(3)	0.3809(8)
C11	0.6406(9)	0.2289(5)	0.2444(12)
H21	−0.3066	0.4336	0.9160
H22	−0.2417	0.5163	0.9793
H23	−0.1322	0.4475	1.0210
H41	−0.4180	0.4062	0.2070
H42	−0.4658	0.4941	0.2426
H43	−0.4852	0.4371	0.3929
H5	0.3079	0.3321	0.3960
H7	0.1988	0.1276	0.5146
H8	−0.0388	0.1687	0.6115
H9	−0.0889	0.2913	0.6107
H111	0.7207	0.2187	0.3320
H112	0.6856	0.2677	0.1717
H113	0.6270	0.1853	0.1747

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

TABLE II. Selected Bond Distances (Å) and Angles (°)

Cu–O(1)	1.978(2)	Cu–O(1)–C(1)	123.4(2)
Cu–O(2)	1.975(2)	Cu–O(2)–C(1)	122.5(2)
Cu–O(3)	1.979(3)	Cu–O(3)–C(3)	120.7(3)
Cu–O(4)	1.964(3)	Cu–O(4)–C(3)	125.8(3)
Cu–N(1)	2.173(3)	O(1)–C(1)–O(2)	125.3(3)
Cu–Cu′	2.607(1)	O(3)–C(3)–O(4)	124.8(4)
C(1)–O(1)	1.260(4)	N(1)–Cu–O(1)	94.5(1)
C(1)–O(2)	1.232(4)	N(1)–Cu–O(2)	96.9(1)
C(3)–O(3)	1.270(5)	N(1)–Cu–O(3)	95.9(1)
C(3)–O(4)	1.229(5)	N(1)–Cu–O(4)	95.6(1)

it may be indicative of an underestimation of the uncertainties, or of imperfect decay and absorption corrections. No abnormal intermolecular interactions are observed. An ORTEP drawing of **3** is given in Fig. 1.

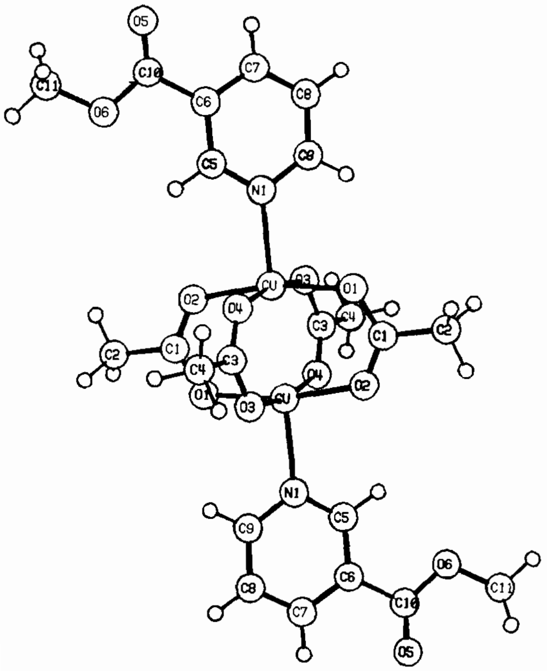


Fig. 1. ORTEP drawing of **3**.

Supplementary Material

Tables of distances and angles, anisotropic thermal parameters, and structure factor amplitudes (13 pp.) are available from the authors on request.

Acknowledgements

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