volatile compounds were removed in vacuo,[12] and THF (10 mL) was added to the residue. In a separate flask $Ni(PPh_3)_4$ was prepared from anhydrous $Ni(acac)_2$ (1 mmol), diisobutylaluminum hydride (1 mmol), triphenylphosphine (4 mmol), and 15 mL of THF. To the mixture containing the β-ethoxyethenylzirconium derivative prepared above were added sequentially the supernatant solution of $Ni(PPh_3)_4$ and 2.04 g (10 mmol) of iodobenzene. After stirring the reaction mixture for 12 h at room temperature, GLC examination of a quenched aliquot indicated the formation of (E)-β-ethoxystyrene in 99% yield. After extraction with diethyl ether, washing with water, and drying, distillation provided 1.12 g (76%) of essentially pure (E)-β-ethoxystyrene: bp 70–72 °C (1.6 mm); ^1H NMR ($CDCl_3$, Me_4Si) δ 1.27 (t, J = 7 Hz, 3 H), 3.80 (q, J = 7 Hz, 2 H), 5.83 (d, J = 13 Hz, 1 H), 6.97 (d, J = 13 Hz, 1 H), and 7.20 (broad s, 5 H) ppm; ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.80, 65.40, 106.03, 125.11, 125.56, 128.58, 136.68, and 147.96 ppm; IR (neat) 1630 (s), 1180 (s), 930 (m), 920 (m), 750 (s), 690 (s) cm^{-1}.

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(7) The use of 1 equiv each of these reagents has resulted in somewhat diminished and variable yields.

(8) A minor amount (<ca. 20%) of a by-product having a slightly shorter GLC retention time (SE-30) than that of (E)-p-(1-hexenyl)anisole was detected in the reaction mixture obtained by the reaction of p-iodoanisole and the (E)-1-hexenylzirconium reagent. Although this by-product, which is neither bianisyl nor 5,7-dodecadiene, may well be a cyclopentadiene derivative, its isolation and identification have not yet been successful. Interestingly, it was readily and completely destroyed during the workup. Consequently, it did not interfere with the isolation of the desired product.

(9) Other functional groups have not so far been tested. However, it has been reported that organozirconium derivatives obtained by the hydrozirconation with $Cl(H)ZrCp_2$ are generally inert to ketones, aldehydes, and alkyl halides, sulfates, and sulfonates.[4]

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(11) Our preliminary results indicate that the difficulty observed with internal alkynes may be overcome by adding a suitable second catalyst such as $ZnCl_2$. This possibility is being investigated in detail in our laboratory.

(12) In most cases the remaining alkynes were removed in this step. However, we have also found that the presence of alkynes does not interfere with the cross-coupling reaction.

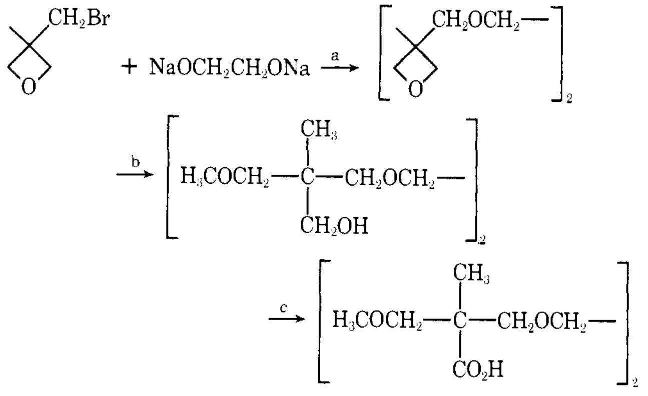
Ei-ichi Negishi,* David E. Van Horn
Department of Chemistry, Syracuse University
Syracuse, New York 13210
Received December 21, 1976

Dimeric Copper(II) Complexes Derived from 2,9-Bis(methoxymethyl)-2,9-dimethyl-4,7-dioxydecanedioic Acid. Formation of a Macrocyclic Chelate

Sir:

The complexation of multivalent cations by polyoxygenated ligands, including polyhydroxy derivatives,[1] multidentate macrocyclic compounds,[2,3] and carboxylates has been the subject of extensive studies, in particular because of the biological interest of such systems, and possible technological applications. However, relatively little work appears to have been done on ether–carboxylic acids.[4–9] Since the ether function(s) in such ligands would usually be expected to form rather labile bonds to metal cations, the resulting complexes, even if sufficiently stable to be isolated, might dissociate readily to yield coordinatively unsaturated species having catalytic activity.

Scheme I. Synthesis of 2,9-Bis(methoxymethyl)-2,9-dimethyl-4,7-dioxydecanedioic Acid.



1

Table I

	3ai	**3bii**	**3cii**
a	11.506 (4) Å	11.230 (4) Å	14.593 (1) Å
b	7.149 (2)	9.940 (4)	10.747 (1)
c	13.085 (3)	10.954 (4)	11.894 (2)
α	101.01 (1)°	112.16 (3)°	75.025 (6)°
β	114.06 (2)°	107.26 (3)°	115.011 (6)°
γ	90.85 (2)°	81.22 (3)°	99.567 (6)°
Formula	$C_{28}H_{52}Cu_2O_{18}$	$C_{38}H_{58}Cu_2N_2O_{16}$	$C_{64}H_{78}Cu_2O_{16}P_2$
Z	1	1	1
No. of obsd ($>3\sigma$) reflections	2681	2368	3038
Current R factor	0.085	0.104	0.094

[a] Δ, *tert*-amyl alcohol solvent. [b] Reflux in methanol–H_2SO_4 catalyst. [c] HNO_3. The product was purified as the dimethyl ester, bp 123 °C (0.01 mmHg). Subsequent reactions were performed on the acid obtained as a viscous gum on hydrolysis of the ester.

In the course of a study of complexes of ether–carboxylic acids, we have prepared 2,9-bis(methoxymethyl)-2,9-dimethyl-4,7-dioxydecanedioic acid (**1**; H_2Y) as a mixture of diastereoisomers by the route outlined in Scheme I. Heating **1** with an equimolar quantity of copper(II) acetate monohydrate in refluxing benzene, followed by distillation to azeotrope water and acetic acid gave a greenish blue-black solution. Column chromatography (silica gel) of this solution, and fractional crystallization (aqueous acetone) of the material eluted with benzene and with ether–benzene (1:3) gave two products, both of which have empirical formula $CuY{\cdot}H_2O$.[10] The major product (**3ai**) crystallized as thin green parallelograms (mp ~183 °C),[11] while the minor product (**3aii**) gave irregular blue prisms (mp ~170 °C).[11] Both products separately dissolved in refluxing benzene to give blue-black solutions from which the water could be removed by azeotropic distillation. Addition of acetonitrile followed by cyclohexane to these solutions resulted in the slow deposition of the appropriate $CuY{\cdot}H_2O$ on standing in air for 1 or 2 days. The crystals of the major isomer **3ai** thus produced were better

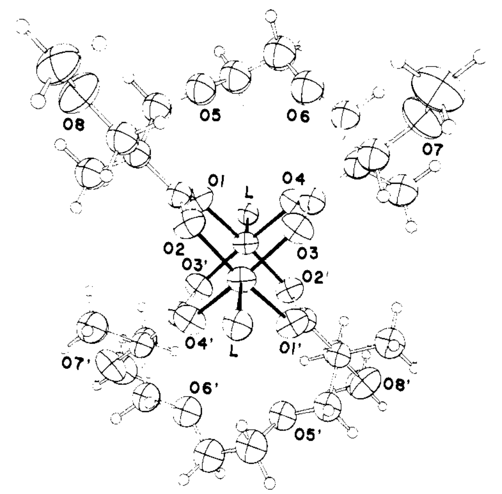
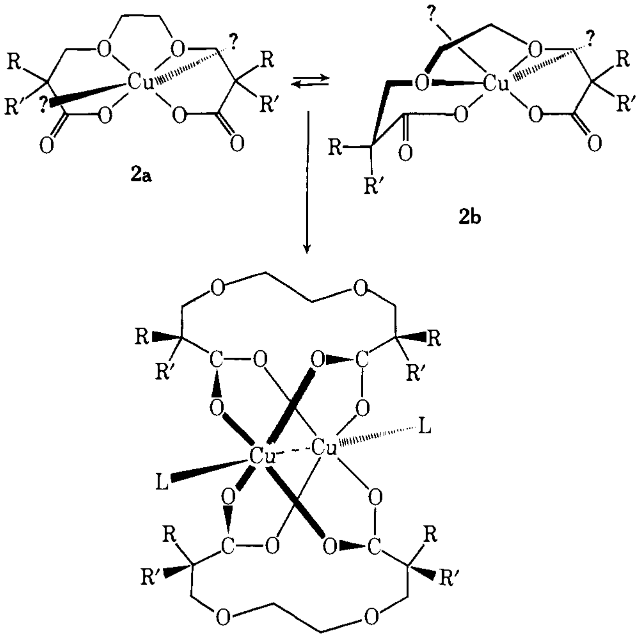


Figure 1. A view of the **3bii** molecule. For clarity, only the coordinated nitrogens of the pyridine moieties are shown.

formed than those obtained from aqueous acetone, and their structure was determined by x-ray analysis (vide infra); the crystals of the minor isomer **3aii** were unsuitable for structure determination. However, treatment of the benzene solutions obtained from **3ai** and **3aii** with pyridine or triphenylphosphine gave green solutions from which complexes of empirical formulae CuY·pyr (major, **3bi**, mp 132–133 °C *ex.* cyclohexane; minor, **3bii**, mp 156–158 °C *ex.* benzene-cyclohexane)[10] and CuY·PPh$_3$ (major, **3ci**, mp 131–132 °C; minor, **3cii**, mp 147.5–148 °C; both *ex.* cyclohexane)[10] were isolated. Recrystallization of both minor products (**3bii** and **3cii**) from ethanol gave crystals whose structures have been determined by x-ray crystallography.



2a

2b

3a,L = H$_2$O; 3b,L = pyridine; 3c,L = triphenylphosphine

(i) mixture of meso and *dl* ligands; R and R^1 are different and may be either CH$_3$ or CH$_2$OCH$_3$

(ii) meso ligand only; R = CH$_3$, R^1 = CH$_2$OCH$_3$

Compounds **3ai**, **3bii**, and **3cii** crystallize in the triclinic space group $P\bar{1}$ with one dimeric unit centered about the crystallographic center of symmetry. Three-dimensional intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer using graphite monochromated Mo Kα radiation. The structures were solved by the Patterson-F_o Fourier method and refined by full-matrix least-squares calculations. Crystal data and refinement parameters are summarized in Table I. In **3ai**, the -OCH$_2$CH$_2$O- segment of the ligand backbone is disordered over two equally populated conformations while the relative configurations at the asymmetric α carbon atoms are consistent with a mixture of *d*, *l*, and meso forms. Compounds **3bii** and **3cii** are both ordered, with the ligand present only in the meso form. Figure 1 shows a view of **3bii** and the meso configurations. In all three molecules the nature of the carboxylic cage about the copper atoms is very similar to that found in copper acetate dihydrate[12] with Cu···Cu distances 2.62 (1) in **3ai**, 2.654 (5) in **3bii**, 2.651 (5) Å in **3cii**, Cu–O (carboxylate) distances in the range 1.85–2.03 Å and Cu–O (water) 2.24 (3) Å; in the pyridine and triphenylphosphine complexes the Cu–N and Cu–P distances are respectively 2.175 (8) and 2.561 (8) Å.

Earlier work on copper(II) complexes of hydroxy- or alkoxycarboxylic acids[9] has indicated that whereas α- or β-hydroxycarboxylates, or α-alkoxycarboxylates form chelates, β-alkoxycarboxylates in aqueous solution act only as monodentate ligands. This might lead one to predict that **1** should show little or no tendency to form chelates with Cu(II) involving the ether oxygens. However, formation from **1** of a chelate involving coordination of both carboxylate groups and the backbone ether oxygens (**2a** or **2b**) would result in a relatively favorable sequence of six-, five-, and six-membered rings.[13] The fact that the complexes obtained above are dimeric rather than polymeric (cf., e.g., copper(II) succinate dihydrate[14]) may indicate that the chelate **2a,b** is formed as an intermediate. Dimerization to **3** may then occur via displacement of the coordinated ether oxygens.

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George Ferguson,* Alan J. McAlees, Robert McCrindle
Roderic J. Restivo, Paul J. Roberts
Chemistry Department, University of Guelph
Guelph, Ontario, Canada

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Preferential Inhibition of α-Chymotrypsin by the D Form of an Amino Acid Derivative, *N'*-Isobutyryl-*N*-benzyl-*N*-nitrosophenylalaninamide (Ia)[1]

Sir:

We recently reported an irreversible inhibition of α-chymotrypsin by substrates (e.g., Ia and II) that produce carbonium ions.[2] *N'*-Isobutyryl-*N*-nitroso-*N*-benzylphenylala-