man No. 1 paper in solvent system (C) 2-propanol-aqueous ammonia-water (7:1:2). Electrophoresis was carried out on Whatman No. 1 paper in 0.1 M TEAB buffer at 21 V/cm. ^{31}P NMR measurements performed in pyridine solutions with H_3PO_4 as an external standard. Negative chemical shift values are assigned for compounds absorbing at the lower field than H_3PO_4. Field desorption-mass spectrometry was performed on Varian MAT-7 machine.

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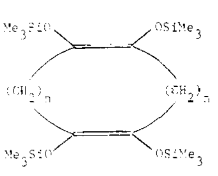
Macrocyclic Compounds with Two 1,3-Diketone Units in the Ring. Synthesis and Transition Metal Complexation

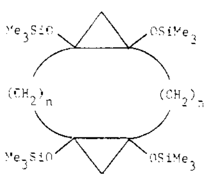
Sir:

The complexation of metal ions by multidentate macrocyclic compounds has been a subject of considerable interest. Recently, Cram and coworkers reported syntheses of cyclic acetylacetone hosts and their affinities for divalent ions.[1] We now wish to report a new and versatile synthesis of macrocyclic compounds (**3**), in which two 1,3-diketone units are symmetrically located in the ring, and their complex formation with transition metal ions such as Cu, Ni, and Co.

The synthesis of the macrocyclic tetraketones **3** started with tetrakis(trimethylsilyloxy)cycloalkadienes (**1**), cyclic silylacyloin dimers, which are derived from the silyl-acyloin condensation[2] of aliphatic dicarbo esters such as dimethyl nonanedioate, dimethyl decanedioate, dimethyl dodecanedioate, and dimethyl tetradecanedioate. Cyclopropanation of **1** with diethylzinc and methylene diiodide afforded tetrakis(trimethylsilyloxy)tricycloalkanes (**2**), which were then treated with $Fe^{III}Cl_3$ in DMF[3] to produce the desired macrocyclic tetraketones **3** in satisfactory yields.



1



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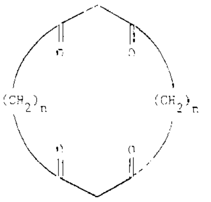
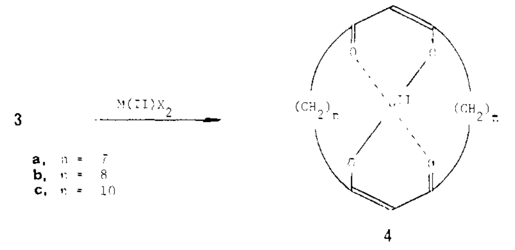


3

a, n = 7
b, n = 8
c, n = 10
d, n = 12

A typical experimental procedure for the preparation of the macrocyclic tetraketones **3** is as follows. Under a nitrogen atmosphere, 40.2 g (150 mmol) of methylene diiodide was added dropwise to a stirring mixture of 16.5 g (26 mmol) of **1b** and 15.7 g (130 mmol) of diethylzinc in 100 mL of benzene at room temperature. The mixture was then heated at reflux for 3 h. The standard workup of the reaction mixture[4] gave 12.5 g of a viscous liquid (**2b**), whose IR spectrum exhibited an absorption band at 3050 cm^{-1} characteristic of cyclopropane ring at the expense of a band at 1665 cm^{-1} ascribable to the carbon-carbon double bond of the starting material of **1b**. The viscous liquid of **2b** without further purification was subjected to the $Fe^{III}Cl_3$ induced ring enlargement reaction;[3] i.e., 12.5 g (19 mmol) of **2b** was added dropwise to a solution of 12.4 g (76 mmol) of anhydrous $Fe^{III}Cl_3$ in 40 mL of DMF at room temperature, and, then, the mixture was heated with stirring at 65 °C for 4 h. The reaction mixture was poured into 10% HCl aqueous solution and extracted with chloroform. The chloroform extract was washed with water, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica gel eluting with chloroform to furnish 4.4 g of 22-membered cyclic tetraketone **3b** (47% yield based on **1b** used) as a keto-enol tautomer mixture. The structure of **3b** was confirmed by elemental analysis[5] and spectral data: IR (neat) 1710, 1610 cm^{-1}; UV ($CHCl_3$) 275 nm (ϵ 5500); NMR ($CDCl_3$ with Me_4Si) δ 0.90–2.00 (br s, 24 H), 2.00–2.60 (m, 8 H), 3.55 (s) + 5.55 (s) + 15.0 (br s) = 4 H; mass spectrum M^+ 364. Similarly, 20-, 26-, and 30-membered cyclic tetraketones **3a, 3c,** and **3d** were synthesized in 33, 43, and 35% isolated yields from tetrakis(trimethylsilyloxy)cycloalkadienes **1a, 1c,** and **1d,** respectively.

CPK molecular model indicated that the macrocyclic tetraketones **3** thus prepared are capable of taking a conformation in which the four carbonyl oxygens are directed toward the inside of the ring and are on a same plane with a cavity large enough to take up some transition metals. Now it was found that 1:1 chelating metal complexes (**4**) were isolated in the reaction of **3a, 3b,** and **3c** with transition metals such as Cu^{II}, Ni^{II}, and CO^{II}. To a solution of 100 mg (0.55 mmol) of anhydrous $Cu^{II}(OAc)_2$ in 10 mL of ethyl alcohol was added 200 mg (0.55 mmol) of **3b** in 3 mL of ethyl alcohol at room temperature and the mixture was stirred for 1 h under nitrogen. A precipitated light blue solid (230 mg) was collected and recrystallized from benzene. The solid was assigned to be 1:1 chelating Cu^{II} complex (**4b**·Cu) by the following spectral data and elemental analysis.[5] IR ((KBr disk) 1565, 1515 cm^{-1})) and UV (($CHCl_3$ solvent) λ_{max} 295 nm (ϵ 9500), 250 (9000)) spectra are similar to those of $Cu^{II}(acac)_2$. Mass spectrum exhibited four parent peaks at 425, 426, 427, and 428 with relative intensity of 100:23.86:47.68:10.51 due to the isotopic distribution, which is consistent with calculated value[6] based on the 1:1 chelating Cu^{II} complex **4b**·Cu. According to the same procedure, 1:1 chelating Cu^{II} complexes **4a**·Cu and **4c**·Cu were prepared.



4

The related nickel(II) and cobalt(II) complexes (**4**·Ni and **4**·Co) were prepared by the reaction of **3** with anhydrous $Ni^{II}Cl_2$ and with anhydrous $Co^{II}Cl_2$ in the presence of triethylamine.

Detailed structure of the 1:1 chelating metal complexes **4**·Cu, **4**·Ni, and **4**·Co must await x-ray analysis.

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cloalkadienes (**1**) were prepared according to the following procedure. To a suspension of sodium dispersion (0.45 g-atom) and trimethylchlorosilane (0.5 mol) in xylene (300 mL), dimethyl decanedioate (0.1 mol) in xylene (30 mL) was added dropwise with vigorous stirring over 3 h at 40–50 °C. Then the mixture was heated at 80 °C for 3 h and allowed to stand overnight at room temperature. After the reaction mixture was filtered, the filtrate was distilled in vacuo. Removal of 1,2-bis(trimethylsilyloxy)cyclodecene by Kugelrohr distillation left a viscous liquid, which was slowly solidified and recrystallized from ether to give pure **1b**, mp 89–90 °C (lit.[2a] mp 90–90.5 °C), in 47% yield. Compounds **1a**, **1c**, and **1d** were separated from 1,2-bis(trimethylsilyloxy)cyclononene, 1,2-bis(trimethylsilyloxy)cyclododecene, and 1,2-bis(trimethysilyloxy)cyclotetradecene, respectively, by Kugelrohr distillation and subjected to the subsequent cyclopropanation without further purification.

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(6) Calculated relative intensity: 425 (100), 426 (24.39), 427 (48.07), 428 (11.06).

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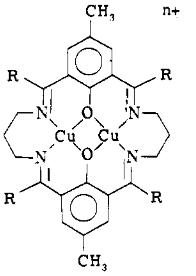
Binuclear Complexes of Macrocyclic Ligands. A Mixed-Valence Copper(II)-Copper(I) Complex which Exhibits Unusual Temperature-Dependent Behavior

Sir:

Macrocyclic ligands can provide transition metals with unusual ligand environments and consequent novel chemical properties: high and low oxidation states are often stabilized;[1] ligand lability is lessened by the chelating effect;[2] several metal atoms may be held in close steric proximity within the same molecule.[3] Capitalizing on these properties of macrocyclic ligands we are studying the behavior of binuclear copper complexes as models for copper-containing proteins.[4] Herein we report preliminary observations on two mixed-valence, copper(II)-copper(I), macrocyclic ligand complexes, one of which exhibited unusual temperature-dependent behavior.

Condensation of 5-methyl-2-hydroxyisophthalaldehyde with 1,3-diaminopropane in the presence of $Cu(ClO_4)_2 \cdot 6H_2O$ yielded the binuclear copper(II) complex, $Cu^{II}Cu^{II}L$, **1**.[5,6] We



1, Cu(II)-Cu(II), n = 2, R = H
2, Cu(II)-Cu(I), n = 1, R = H
3, Cu(II)-Cu(I) (CO), n = 1, R = H
4, Cu(II)-Cu(I), n = 1, R = CH_3

have not been successful in reducing the complex with chemical reducing agents. Cyclic voltammetry in DMF,[7] however, revealed two quasi-reversible reduction waves ($E_1^f \simeq -0.52$ V, $E_2^f \simeq -0.91$ V, $n_1 = n_2 = 1.0 \pm 0.1$) by CPE).[8] Electrolysis of green solutions of **1** (-0.7 V, CH_3CN/N_2, $n = 1.0 \pm 0.1$) resulted in a dark brown solution. A nearly black solid, corresponding to the formula $Cu^{II}Cu^{I}L(ClO_4)$, **2**,[6] was precipitated from solution by the addition of Et_2O. Saturation of the electrolysis solution with CO followed by addition of Et_2O led to precipitation of a CO adduct, $Cu^{II}Cu^{I}L(CO)ClO_4$, **3**,[6,10] (ν_{CO} 2065 cm^{-1}), presumably containing five-coordinate copper(I).

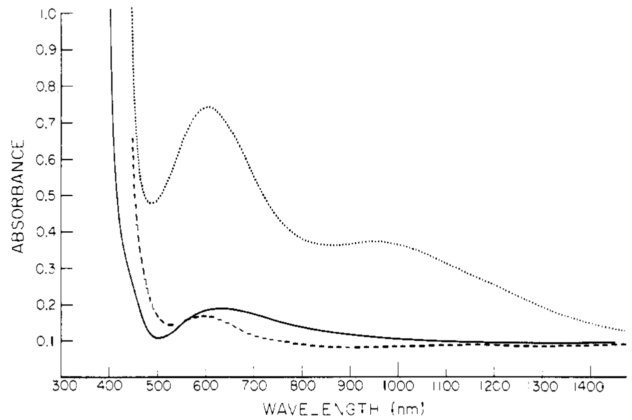


Figure 1. Electronic absorption spectra in methanol of $Cu^{II}_2L(ClO_4)_2(H_2O)_2$, **1** (—); $Cu^{II}Cu^{I}LClO_4$, **2** (· · · ·) under helium; $Cu^{II}Cu^{I}(CO)LClO_4$, **3** (– – –) under carbon monoxide. $[Cu^{II}_2] = 1.15 \times 10^{-3}$ M; $[Cu^{II}Cu^{I}] = [Cu^{II}Cu^{I}(CO)] = 1.10 \times 10^{-3}$ M.

Representative electronic absorption spectra of **1**, **2**, and **3** are shown in Figure 1. All three complexes exhibited intense absorptions in the 350–400-nm region (ϵ 10 000–15 000, presumably ligand absorption) and a weaker band at ~600 nm. Since only the 350–400-nm band was observed in the zinc complex $Zn^{II}Zn^{II}L(ClO_4)_2(H_2O)_2$,[6] we tentatively assign the 600-nm absorptions in **1**, **3**, and **2** (in part) to a ligand field copper(II) transition.[12] Most notable in the spectra was a broad band in the near infrared seen only for **2**. We tentatively assign this as an intervalence-transfer transtion (IT) (copper(II)-copper(I) → copper(I)-copper(II)*).[13] The position of the IT band maximum appeared to be dependent on the solvent donor properties. In noncoordinating CH_2Cl_2 the band was at ~1200 nm ($\epsilon \simeq 80$), while in weakly coordinating CH_3OH, $(CH_3)_2CO$, and DMF the band shifted to ~900 nm. In CH_3CN, which appears capable of forming five-coordinate copper(I) adducts,[9-11] no IT band was observed.

The addition of CO to $Cu^{II}Cu^{I}L$, **2**, to give the carbonyl adduct, $Cu^{II}Cu^{I}L(CO)$, **3**, was essentially complete (in CH_3OH, $(CH_3)_2CO$, DMF, CH_3CN, CH_2Cl_2) as monitored by electronic absorption spectroscopy and cyclic voltammetry.[14] For example, addition of CO to bluish green solutions of **2** (CH_3OH) led to yellow solutions with the electronic spectra of **3** (Figure 1). The lack of an observable IT band for **3** appears consistent with the spectra of **2** in donor solvents; i.e., CO adduct formation may shift the IT band to high energies where it is masked by ligand absorption.

Solution EPR spectra for $Cu^{II}Cu^{I}L$, **2** (Figure 2), consisted of seven lines, consistent with interaction of the odd electron with both copper centers ($I = 3/2$). Internally consistent hyperfine splittings in both solvents imply the presence of only a single EPR active species. In contrast frozen solutions at liquid-nitrogen temperature exhibited four-line anisotropic spectra (CH_2Cl_2 or CH_3CN).[15] Similarly, addition of CO to solutions of **2** resulted in a solution of **3** (by electronic spectra) and an EPR spectrum having only four lines (25 °C, CH_2Cl_2). These four-line spectra, whether from frozen solutions of **2** or solutions of **3** at 25 °C, are consistent with localization of the odd electron on a single copper center, at least on the relatively slow EPR time scale (10^{-8}–10^{-4} s).[16]

Possible explanations for the temperature-dependent behavior of **2** include (1) axial ligation by ClO_4^- or solvent (CH_3CN or CH_2Cl_2) at low temperature leads to an asymmetric complex comparable with the carbonyl adduct, **3**; or (2) macrocyclic ligand conformational changes which accompany electron exchange (possibly distorted tetrahedral for copper(I)