

a new mixture favoring the less polar isomer **5** by a ratio of at least 20:1 was produced. The spectroscopic studies on the spiro ketals and their acetates established the structure for **5** and **6** as indicated.⁶

Being encouraged by our successful total synthesis of lasalocid A,⁷ we planned to form the crucial carbon-carbon bond between the left and right halves **2** and **3** by aldol reaction. After many unsuccessful attempts, we have found that this aldol reaction is nicely effected by freshly prepared (*i*-C₃H₇)₂NMgBr⁸ in THF and furthermore that the ratio of the two diastereomeric aldols **7** and **8** is sensitive to the reaction temperature. The following ratios of **7** and **8** were observed at the indicated temperature: ~1:1 at 0 °C (71% yield; 90% yield based on the consumed ketone **3**), ~2:1 at -20 °C (60%; 91%), >5:1 at -50 °C (30%; 90%), and >8:1 at -78 °C (21%; 92%). The diastereomeric aldols **7**⁵ (¹H NMR (CDCl₃) δ 3.25 (3 H, s), 3.27 (3 H, s), 3.68 (3 H, s), 4.60 (2 H, s), 7.31 (5 H, s); α²²_D +36.3° (*c* 0.95, CH₂Cl₂)⁹) and **8**⁵ (¹H NMR (CDCl₃) δ 3.25 (6 H, s), 3.67 (3 H, s), 4.61 (2 H, a very close AB), 7.30 (5 H, s); α²²_D +46.1° (*c* 0.52, CH₂Cl₂)⁹) could be separated by preparative layer chromatography (Merck silica gel plate (0.5 mm), ether-pentane (5:4), five developments). Based on Cram's rule, the desired stereochemistry was tentatively assigned to the major aldol, which was later confirmed by successful transformation of **7** into monensin (**1**).

Following the conditions that we established in the model series, we subjected the aldol **7** to the following sequence of reactions: (1) 1 atm of H₂, 10% Pd/C, CH₃OH-AcOH (100:5), RT, 30 min; (2) CSA, wet CH₂Cl₂-Et₂O (3:1), RT, 1 h; (3) 1 N NaOH-CH₃OH (1:5), 60 °C, 1 h. Step 2 in this sequence was required to equilibrate the spiro ketal center and also to hydrolyze the tertiary methoxy group at the C(25)² position. Preparative layer chromatography (Merck silica gel plate (0.5 mm), ether, three developments) allowed isolation of synthetic monensin (**1**)¹⁰ as its sodium salt. The overall yield from **7** to **1** was 53%. The synthetic substance was found to be identical with natural monensin in every respect (NMR, IR, α_D, mass spectrum, melting point, mixture melting point, TLC).

Acknowledgment. Financial assistance from National Institutes of Health, National Science Foundation, and Hoffmann-La Roche Inc. is gratefully acknowledged.

References and Notes

- (1) Part 6 of the series Synthetic Studies on Polyether Antibiotics. For part 5, see T. Fukuyama, C.-L. J. Wang, and Y. Kishi, *J. Am. Chem. Soc.*, preceding paper in this issue.
- (2) The numbering corresponds to that of monensin.
- (3) For X-ray analysis of silver salt of monensin, see A. Agtarap, J. W. Chamberlin, M. Pinkerton, and L. Steinrauf, *J. Am. Chem. Soc.*, **89**, 5737 (1967), and M. Pinkerton and L. K. Steinrauf, *J. Mol. Biol.*, **49**, 533 (1970); for X-ray analysis of free acid of monensin, see W. K. Lutz, F. K. Winkler, and J. D. Dunitz, *Helv. Chim. Acta*, **54**, 1103 (1971).
- (4) Compound **4** was synthesized by the aldol reaction analogous to **2** + **3** → **7** + (**8**): D. S. Karanewsky, T. Fukuyama, and Y. Kishi, unpublished results.
- (5) Satisfactory spectroscopic data (NMR, mass spectrum, IR, etc.) were obtained for this substance.
- (6) Details of the structure assignment for **5** and **6** will be reported later.
- (7) T. Nakata, G. Schmid, B. Vranesic, M. Okigawa, T. Smith-Palmer, and Y. Kishi, *J. Am. Chem. Soc.*, **100**, 2933 (1978); T. Nakata and Y. Kishi, *Tetrahedron Lett.*, 2745 (1978).
- (8) This base (1.5 M) was prepared from EtMgBr and diisopropylamine in THF at 80 °C and kept at ~50 °C. The aldol reaction was carried out as follows. The aldehyde **2** (prepared from 38.2 mg of the alcohol (see part 2 of this series) just before use) and ketone (21.5 mg) were dissolved in 10 mL of anhydrous THF under an argon atmosphere, and cooled to -50 °C. To this solution was added 100 μL of the freshly prepared base. At ~5-min intervals, additional base (9 × 25 μL) was added. The reaction was monitored by TLC after each addition of the base. After the base was quenched with saturated ammonium chloride solution at -50 °C, the products were extracted with ether and then with methylene chloride. Preparative layer chromatography (Merck silica gel (0.5 mm), ether-pentane (5:4), five developments) gave 11.1 mg of **7** (30% yield; 90% yield based on the consumed **3**), 2.0 mg of **8** (contaminated by an unknown compound), and 14.3 mg of the recovered ketone **3**.
- (9) It takes some time for this substance to give the steady rotation, perhaps

- owing to the phenomenon similar to mutarotation known for carbohydrates.
 (10) We are indebted to Dr. Chamberlin, Eli Lilly & Co., and Dr. Westley, Hoffmann-La Roche Inc., for samples of sodium salt of monensin.

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Synthesis of Monomeric Niobium- and Tantalum-Benzene Complexes and the Molecular Structure of Ta(η⁵-C₅Me₅)(C₆H₄)Me₂

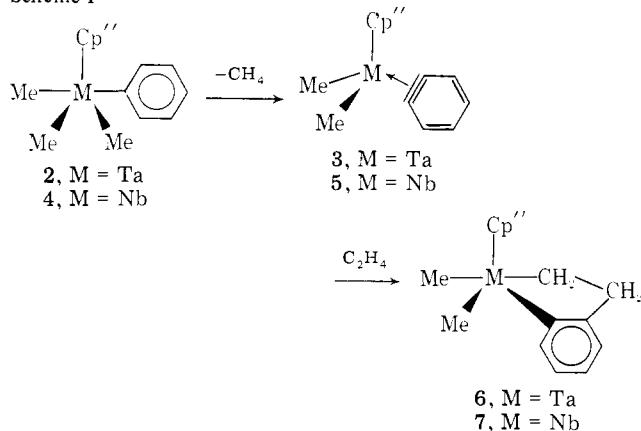
Sir:

Many transition metal complexes contain organic ligands which are highly reactive or unknown in the free state (e.g., cyclobutadiene,¹ trimethylenemethane,² carbenes,³ and small-ring acetylenes⁴). A benzyne (C₆H₄) complex has been postulated as an intermediate in the thermal decomposition of Ti(η⁵-C₅H₅)₂(C₆H₅)₂ on the basis of labeling and trapping experiments,⁵ and recent results by Erker⁶ support the formation of a benzyne intermediate; Zr(η⁵-C₅H₅)₂(C₆H₄), in the thermal exchange of aryl groups between Zr(η⁵-C₅H₅)₂(aryl)₂ and aromatic solvents. To our knowledge, however, no compounds containing a benzyne molecule η² bonded to a single transition metal have been isolated.⁷ Our studies of metallocyclopentane complexes^{1,2} led us to develop a synthesis of tantalum-olefin complexes, Ta(η⁵-C₅Me₅)(CH₂=CHR)Cl₂, by decomposition of thermally unstable dialkyl complexes, Ta(η⁵-C₅Me₅)(CH₂CMe₃)(CH₂CH₂R)Cl₂ (R = H, Me).¹³ We now report the extension of this principle, a form of the β-hydride elimination process by which many transition metal alkyl complexes decompose,¹⁴ to the preparation of stable benzyne complexes.¹⁵

Ta(η⁵-C₅Me₅)(CH₂CMe₃)Cl₂¹³ reacts slowly (~24 h) with 1 equiv of Zn(C₆H₅)₂ in benzene to give neopentane and a dark brown solution containing Ta(η⁵-C₅Me₅)(C₆H₄)Cl₂ (**1**); no intermediates can be observed by ¹H NMR. Ta(η⁵-C₅Me₅)(C₆H₄)Cl₂ can be isolated as yellow crystals in 44% yield by removing the benzene in vacuo and recrystallizing the gummy residue from toluene at -30 °C. The ¹H NMR spectrum of **1** (τ, C₆H₆) shows a singlet for the η⁵-C₅Me₅ group at 8.26 (relative area 15) and a symmetric AA'BB' pattern consisting of two multiplets at 2.07 and 2.78 (relative area 4), consistent with its formulation as a benzyne complex. Since **1** is not soluble enough for ¹³C NMR or a cryoscopic molecular weight determination, we sought a more soluble derivative.

Adding 1 mol of phenyllithium to a suspension of Ta(η⁵-C₅Me₅)Me₃Cl¹³ in ether at -78 °C initially produces a ho-

Scheme I



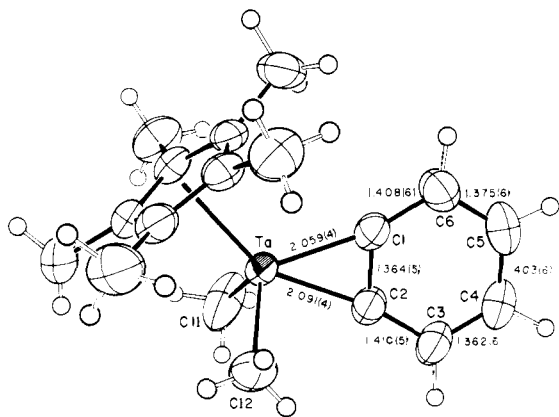


Figure 1. Molecular structure of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_6\text{H}_4)\text{Me}_2$.

mogeneous yellow solution; when this is warmed to room temperature LiCl precipitates from solution. Removal of the ether in vacuo, followed by recrystallization from pentane-toluene (80:20), gives yellow crystalline $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_6\text{H}_5)\text{Me}_3$ (**2**) in 71% isolated yield.¹⁶ Unlike the presumed intermediate in formation of **1** ($\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{CMe}_3)(\text{C}_6\text{H}_5)\text{Cl}_2$), **2** is fairly stable thermally. It requires 30 min at 120 °C in chlorobenzene for **2** to decompose to give methane (by GLC) and $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_6\text{H}_4)\text{Me}_2$ (**3**) (Scheme 1). Pentane-soluble **3** can be obtained as pale yellow, relatively air-stable crystals in 80% yield by removing the chlorobenzene in vacuo and recrystallizing the residue from pentane at -30 °C.¹⁷ The ¹H NMR spectrum of **3** is similar to that of **1** with an additional peak due to the methyl groups.¹⁷ A cryoscopic molecular weight determination indicated that **3** is a monomer in cyclohexane (calcd, 422; found, 406 ± 20). The ¹H gated-decoupled ¹³C spectrum is also consistent with the formulation of a benzyne complex, the most notable feature being the peak at 230.5 ppm which shows no directly bonded proton coupling, and which is therefore assigned to the metal-bonded carbon atoms of the benzyne ligand.¹⁸ Since the 270-MHz ¹H and 67.89-MHz ¹³C spectra of **3** are temperature invariant down to -80 °C, we believed that the benzyne ligand was bound so as to complete the pseudo-tetragonal-pyramidal coordination sphere.

The niobium analogue of **3** can be prepared by a similar procedure from $\text{Nb}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_6\text{H}_5)\text{Me}_3$ (**4**, Scheme 1); **4** is significantly less stable than **2** and decomposes at 30 °C ($t_{1/2} \approx 5$ h) to give yellow, crystalline $\text{Nb}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_6\text{H}_4)\text{Me}_2$ (**5**) in 87% isolated yield. Its ¹H and ¹³C NMR spectra are similar to those of **3**;²⁰ the α -carbon atom resonance of the benzyne ligand is found at 213 ppm and is broadened by coupling to niobium.

Both **3** (at 80 °C) and **5** (at 30 °C) react with ethylene to give the benzotantalocyclopentene complexes, **6** (86% isolated yield)^{21a} and **7** (75% isolated yield), respectively. Their ¹H and ¹³C NMR spectra are characteristic^{21b} and temperature dependent (cf. tantalocyclopentane complexes¹²); ΔG^\ddagger for pseudorotation (interchanging Me and Me') = 13.6 ± 0.5 kcal mol⁻¹ for **6**.²² It is surprising that **3** and **5** do not react more rapidly with ethylene since the reaction of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_2\text{H}_4)\text{Cl}_2$ with ethylene to give $\text{Cl}_2(\eta^2\text{-C}_5\text{Me}_5)\text{-TaCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ is fast, even at -30 °C.¹³

The molecular geometry of $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_6\text{H}_4)\text{Me}_2$ has been determined unequivocally by means of a single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$, with $a = 8.8789$ (12) Å, $b = 9.2365$ (14) Å, $c = 11.3174$ (18) Å, $\alpha = 71.769$ (12)°, $\beta = 76.101$ (12)°, $\gamma = 73.142$ (11)°, $V = 832.2$ (2) Å³, and $\rho(\text{calcd}) = 1.685$ g cm⁻³ for mol wt 422.35, and $Z = 2$. Diffraction data were collected by a θ - 2θ scan technique using a Syntex P2₁ automated diffractometer and were corrected for

absorption via an empirical method based upon a series of ψ scans of close to axial reflections ($\mu = 69.5$ cm⁻¹). The structure was solved by a combination of Patterson, difference-Fourier, and full-matrix least-squares refinement techniques. All atoms, including all hydrogen atoms, were located and their positional and thermal parameters (anisotropic for Ta and C; isotropic for H) refined. The resulting discrepancy indices are $R_F = 2.5\%$ and $R_{wF} = 2.0\%$ for all 3836 reflections with $4^\circ < 2\theta < 55^\circ$ (Mo K α radiation). No reflections were rejected.

The molecular geometry and selected bond distances are shown in Figure 1. The central tantalum atom is linked directly to an η^5 -pentamethylcyclopentadienyl ligand (Ta-C(Cp) distances range from 2.408 (3) to 2.500 (4) Å, averaging 2.452 Å), to two methyl groups (Ta-C(11) = 2.169 (6) and Ta-C(12) = 2.181 (6) Å), and to an " η^2 -C₆H₄" ligand. Surprisingly, the benzyne ligand plane (which makes an angle of 2.3° with the Ta-C(1)-C(2) plane) is oriented essentially perpendicular (85.3°) to the plane of the cyclopentadienyl system. The six-membered ring has a root-mean-square deviation from planarity of only 0.006 Å and the tantalum atom lies 0.078 Å from this plane. A careful survey of carbon-carbon bond distances around the six-membered carbocyclic ring shows a pattern of D_{3h} symmetry—the possible D_{6h} symmetry is broken by a slight, but nevertheless unmistakable, alternation in bond length around the system. The C(1)-C(2) bond length of 1.364 (5) Å is not distinguishable from C(3)-C(4) = 1.362 (6) or C(5)-C(6) = 1.375 (6) Å. However, neither this information nor the Ta-C(1) and Ta-C(2) bond lengths help us decide between a benzyne and *o*-phenylene description, a difference which is undoubtedly more formal than real. Even the fact that the benzyne ligand must be rapidly rotating about the Ta-C(1)-C(2) bond in solution ($\Delta G^\ddagger \leq 9$ kcal mol⁻¹²³) is of little help. Such rotation is well established for acetylene ligands²⁴ and we know that ethylene rotates in $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_2\text{H}_4)\text{Cl}_2$ ($\Delta G^\ddagger_{203} = 9.3 \pm 0.3$ kcal mol⁻¹¹³), but pseudo-tetragonal-pyramidal tantalocyclopentane complexes,^{12b} as well as **6**, **7**, and simple alkyl complexes such as $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_3\text{Cl}$ ¹³ are known to pseudorotate with $\Delta G^\ddagger = 10$ -15 kcal mol⁻¹.

We believe that the orientation of the benzyne ligand is dictated by overlap of the benzene's π -electron system with a low-lying π -type metal orbital which is directed toward the two empty coordination sites in a pseudo tetragonal pyramid. The metal is seriously electron deficient. Delocalization of π electrons throughout the Ta-C₆H₄ system may be part of the reason why **3** and **5** only reluctantly react with ethylene.

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- (15) This type of decomposition reaction may be responsible for the relative scarcity of early transition metal "perphenyl" complexes, $M(\text{phenyl})_x$.^{14b} (See also ref 5 and 6.)
- (16) Calcd for $\text{TaC}_{18}\text{H}_{25}$: C, 52.06; H, 6.66. Found: C, 52.09; H, 6.40. ¹H NMR (τ , C_6D_6): 2.60–3.30 (m, 5, C_6H_5), 8.53 (s, 15, C_5Me_5), 8.87 (s, 9, TaMe_3). The methyl groups are equilibrating rapidly on the NMR time scale at this temperature, presumably by a "reverse" pseudorotation (tetragonal pyramid to tetragonal pyramid; cf. $\text{TaCp}^+\text{Me}_3\text{Cl}$ in text).
- (17) Calcd for $\text{TaC}_{18}\text{H}_{25}$: C, 51.19; H, 5.96. Found: C, 52.10; H, 6.02. ¹H NMR (τ , C_6D_6): 1.50 and 2.48 (AA'BB' pattern, 4, C_6H_4), 8.20 (s, 15, C_5Me_5), 9.79 (s, 6, TaMe_2).
- (18) ¹³C NMR (parts per million downfield of Me_4Si in C_6D_6 , ¹H decoupled): 11.0 (q, ¹J_{CH} = 127 Hz, C_5Me_5), 52.7 (q, ¹J_{CH} = 120 Hz, TaMe_2), 115.3 (s, C_5Me_5), 131.8 (d, ¹J_{CH} = 159 Hz, C_6H_4), 132.4 (d, ¹J_{CH} = 159 Hz, C_6H_4), 230.5 (s, ²J_{CH} = 8 Hz, C_6H_4).
- (19) Red crystalline $\text{Nb}(\text{C}_5\text{Me}_5)_3\text{Me}_3\text{Cl}$ is prepared in 87% yield by the addition of solid LiC_5Me_5 to an ethereal solution of NbMe_3Cl_2 ^{14b} followed after 1 h by filtration and concentration in vacuo. ¹H NMR (τ , C_6D_6): 8.30 (s, 15, C_5Me_5), 8.60 (s, 9, 3Me). Reaction with phenyllithium gives **4** in 60% isolated yield.
- (20) ¹H NMR (τ , C_6D_6): 1.65 and 2.55 (AA'BB' pattern, 4, C_6H_4), 8.22 (s, 15, C_5Me_5), 9.40 (s, 6, NbMe_2). ¹³C NMR (parts per million, CDCl_3 , -40 °C, ¹H decoupled): 10 (s, C_5Me_5), 44 (s, NbMe_2), 115 (s, C_5Me_5), 129 (s, C_6H_4), 130 (s, C_6H_4), 213 (s, C_6H_4).
- (21) (a) Anal. Calcd for $\text{TaC}_{20}\text{H}_{29}$: C, 53.34; H, 6.48. Found: C, 53.42; H, 6.54. (b) ¹H NMR (τ , C_6D_6 , 80 °C, except phenyl protons): 5.92 (t, 2, ²J_{HH} = 6 Hz, $\text{TaCH}_2\text{CH}_2\text{C}_6\text{H}_4$), 7.95 (t, 2, ²J_{HH} = 6 Hz, $\text{TaCH}_2\text{CH}_2\text{C}_6\text{H}_4$), 8.38 (s, 15, C_5Me_5), 9.30 (s, 6, TaMe_2). ¹³C NMR (parts per million, ¹H gated decoupled, C_6D_6): 11.2 (q, ¹J_{CH} = 128 Hz, C_5Me_5), 44.4 (t, ¹J_{CH} = 124 Hz, $\text{TaCH}_2\text{CH}_2\text{C}_6\text{H}_4$), 74.4 (br q, ¹J_{CH} = 123 Hz, TaMe_2), 96.1 (t, ¹J_{CH} = 117 Hz, $\text{TaCH}_2\text{CH}_2\text{C}_6\text{H}_4$), 119.5 (s, C_5Me_5), 124.6 (d, ¹J_{CH} = 160 Hz, C_6H_4), 126.7 (d, ¹J_{CH} = 159 Hz, C_6H_4), 127.3 (d, ¹J_{CH} = 158 Hz, C_6H_4), 137.6 (d, ¹J_{CH} = 163 Hz, C_6H_4), 158.6 (s, C_6H_4), 213.9 (s, C_6H_4).
- (22) At -52 °C two methyl peaks are found at 69.8 and 79.0 ppm in the ¹³C {¹H} NMR spectrum in toluene-*d*₈. $\delta\nu_{\text{in}}$ for the two methyl groups is 138 ± 10 Hz and $k_c = 308 \text{ s}^{-1}$ at $T_c = 288 \pm 10 \text{ K}$ or $\Delta G^\ddagger = 13.6 \pm 0.5 \text{ kcal mol}^{-1}$.
- (23) By ¹³C NMR, if $\delta\nu_{\text{in}}$ is estimated as 70 Hz and $T_c = 193 \text{ K}$, then ΔG^\ddagger (maximum) = 9.2 kcal mol⁻¹. By ¹H NMR, if $\delta\nu_{\text{in}}$ is estimated as 81 Hz, $J_{\text{HH}} = 10 \text{ Hz}$ and $T_c = 178 \text{ K}$, then ΔG^\ddagger (maximum) = 8.4 kcal mol⁻¹.
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Synthesis and Structure of the Imidazolate Bridged Dicopper(II) Ion Incorporated into a Circular Cryptate Macrocycle

Sir:

Discrete imidazolate (im) bridged binuclear metal complexes are of interest to prepare and characterize since units of this kind are known¹ or proposed² to exist in metalloproteins. Previously we described a number of imidazolate bridged dicopper(II) complexes.³ Related bis[methylmercury(II)],⁴ bis[porphyrinatoiron(II)] and -[porphyrinatomanganese(II)],⁵ cobalt and ruthenium ammine,⁶ as well as additional dicopper(II)⁷ compounds are also known. Some of these compounds have been shown to undergo pH dependent imidazolate bridge splitting reactions,^{3,4} of relevance to proposed enzyme mechanisms.⁸ Additional solution studies would be greatly facilitated if the imidazolate bridged bimetallic center were incor-

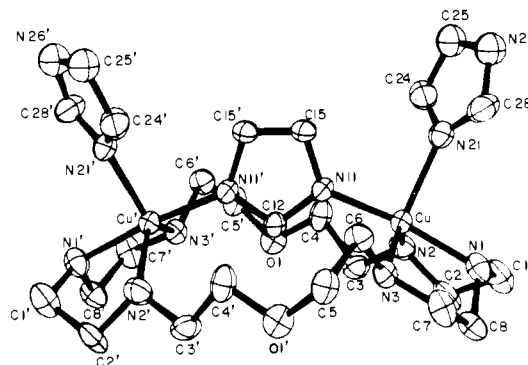
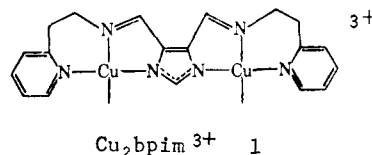
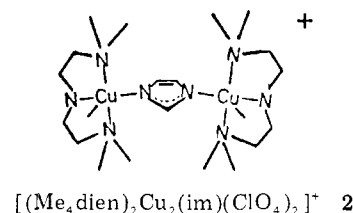


Figure 1. Structure of $[\text{Cu}_2(\text{imH})_2(\text{im})\text{Cu}]^{3+}$ showing the 40% probability thermal ellipsoids. The primed and unprimed atoms are related by a crystallographically required twofold symmetry axis. Selected bond distances (in ångströms; esd, ~ 0.01 Å) follow: Cu-N(1), 2.033; Cu-N(11), 1.946; Cu-N(2), 2.251; Cu-N(3), 2.131; Cu-N(21), 2.133. Selected bond angles (in degrees; esd, $\sim 0.4^\circ$) follow: N(11)-Cu-N(1), 171.5; N(11)-Cu-N(21), 94.2; N(11)-Cu-N(2), 98.9; N(11)-Cu-N(3), 89.6; N(1)-Cu-N(2), 83.2; N(1)-Cu-N(3), 83.0; N(1)-Cu-N(21), 93.7; N(21)-Cu-N(2), 97.6; N(21)-Cu-N(3), 127.9; N(2)-Cu-N(3), 133.1. The copper atom is displaced from the plane defined by N(2), N(3), and N(21) by 0.15 Å toward N(11).

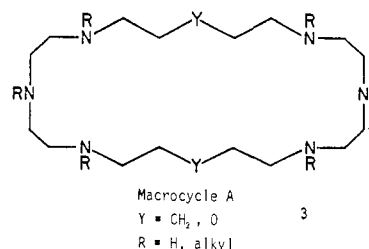
porated into a ligating cavity that would prevent the two metal ions from migrating away from each other when the bridge is broken. The ligand 4,5-bis[2-(2-pyridyl)ethyliminomethyl]imidazolate (bpim) was synthesized for this purpose, but the imidazolate bridge in $\text{Cu}_2\text{bpim}^{3+}$ (**1**) is too stable, remaining



intact down to pH 4.25.^{3a} Examination of the structure of the $[(\text{Me}_4\text{dien})_2\text{Cu}_2(\text{im})(\text{ClO}_4)_2]^+$ cation^{3c} (**2**) suggested that



circular cryptate macrocycles such as **3** (macrocycle A), in which two five-atom chains link the two diethylenetriamine moieties, would be ideally suited to girdle the $[\text{Cu}_2(\text{im})]^{3+}$ ion. Here we report the synthesis and X-ray crystal structure of one such compound, $[\text{Cu}_2(\text{imH})_2(\text{im})\text{Cu}](\text{ClO}_4)_3$.¹⁰



The ligand A¹⁰ was prepared as a colorless oil in 77% yield by detosylation of the monocycle amine tetraosylate (compound **10** in ref 9) using HBr, 40% in acetic acid, in the presence of 12 equiv of phenol at 80 °C for 24 h. A 60 mM solution of the macrocycle in 1.25 mL of methanol was slowly added to 3 mL of a 50 mM methanolic solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. To the resulting deep blue solution was added 1.3 mL of 0.1 N sodium imidazolate in 90% methanol followed by an excess