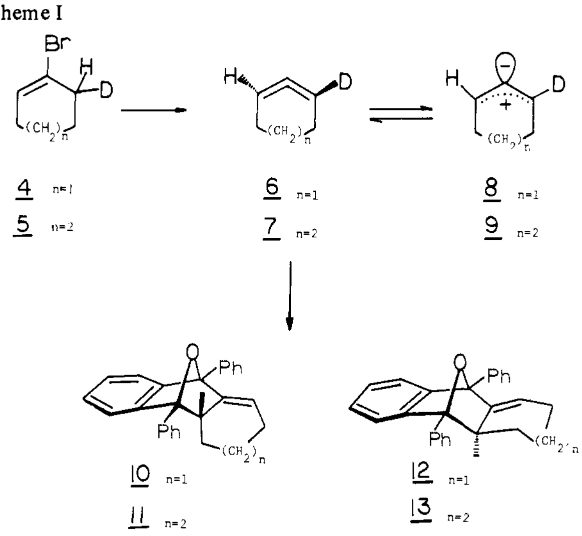
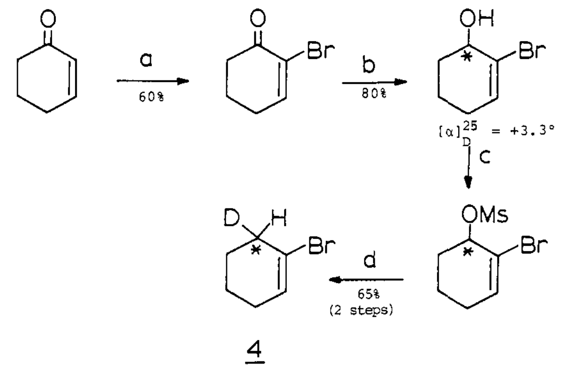
Scheme I

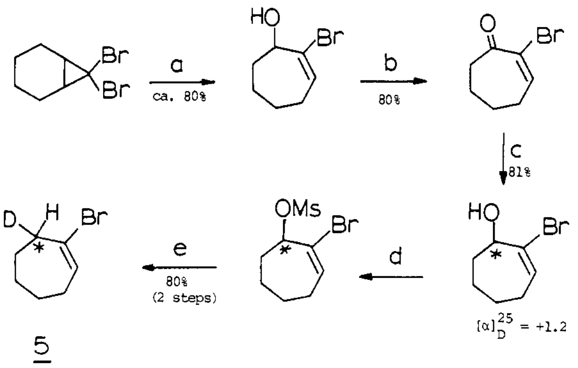


Scheme II[a]



[a] (a) Bromine, collidine.[19] (b) Quinine, LiAlH$_4$. (c) MsCl, NEt$_3$. (d) LiAlD$_4$.

Scheme III[a]



[a] (a) AgClO$_4$, acetone/water (9:1). (b) PCC. (c) Quinine, LiAlH$_4$. (d) MsCl, NEt$_3$. (e) LiAlD$_4$.

would give different enantiomers,[14] should occur at different rates. The intermediates were trapped with 1,3-diphenylbenzo[*c*]furan[7,9,10] to give **10**, **11**, **12**, and **13**.[15] All four adducts are chiral and should therefore show activity if the intermediates were active.[16]

Table I. Optical Activities of Adducts[a]

temp, °C	specific rotation $[\alpha]^{25}{}_D$, deg 12 minor adduct	 10 major adduct	 11 major adduct	solvent and time
53	+1.6 ± 0.11	−0.3 ± 0.09	+0.94 ± 0.06	THF, 20 h,[b] 2 h[c]
80	+0.3 ± 0.2	0.0 ± 0.11		diglyme, 6 h[b]
100	0.0 ± 0.06	0.0 ± 0.06	+0.69 ± 0.06	diglyme, 1 h,[b] 15 min[c]
140			+0.35 ± 0.1	diglyme, 10 min[c]

[a] For all reactions the same concentrations of all starting materials were used. [b] For 1-bromo-6-deuteriocyclohexene. [c] For 1-bromo-7-deuteriocycloheptene.

Optical activities of the four adducts (carefully chromatographed but not recrystallized) are given in Table I. From the results at 53 °C it is clear that both the initially formed and reacting intermediates from both **4** and **5** must be chiral and therefore cannot be adequately represented by intermediates with electrons distributed as in **1**, **2**, or **3** but are consistent with structures **6** and **7**. The effect of temperature on optical activity is also instructive. In the case of 1-bromocycloheptene, the optical activity drops off with an increase in temperature at a rate that is consistent with a simple temperature effect[17] on k_H/k_D. However, in the case of 1-bromocyclohexene, the loss of activity is much too rapid to be explained by this simple effect. We therefore suggest that in the range of 80 °C isomerization of **6** to **8** is competitive with trapping by 1,3-diphenylbenzo[*c*]furan; the unimolecular racemization is expected to be more sensitive to temperature than the competitive bimolecular Diels-Alder reaction. At this time we do not feel that such a racemization mechanism is required for 1,2-cycloheptadiene.[18]

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation.[20]

Supplementary Material Available: Accompanying Experimental Section with syntheses of compounds (4 pages). Ordering information is given on any current masthead page.

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(14) This would be true only if the elimination is concerted. To our knowledge the mechanism of elimination from small-ring 1-halocycloalkenes has not been studied. However, it was a priori unlikely that it would be E1cb and this is confirmed by the results reported here. It may also be noted that concerted elimination *must* be cis; trans is sterically impossible.

(15) No cycloalkyne adducts were observed.

(16) Activity in the adduct is in reality a result of asymmetric induction in that an enantiomer of the allene should attack one face of the diene faster than the other.

(17) Shiner, V. J.; Smith, M. L. *J. Am. Chem. Soc.* **1961**, *83*, 593-8.

(18) Determination of the effect of changing the concentration of the diene on the activity of the adduct could, in principle, provide a less equivocal test for competitive unimolecular racemization and bimolecular cycloaddition. Unfortunately, to date, experimental difficulties have precluded applying this test to either **4** or **5**.

(19) Bouvell, F. G.; Wellman, K. M. *J. Org. Chem.* **1963**, *28*, 2544.

(20) We also acknowledge with gratitude the suggestion of Professor Ronald Breslow that chirality could be a way to probe the cycloheptatrienylidene-cycloheptatetraene question. The work reported here was an outgrowth of the latter which will be reported at a later time.

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Macrocyclic Inclusion Complexes. Synthesis, Complexation, and X-ray Crystal Structures of Binuclear Cation Complexes of Dipyridine Crown Ethers[1]

Sir:

Over the past decade, a myriad of novel synthetic macrocyclic ligands have been designed to complex metal cations. Generally

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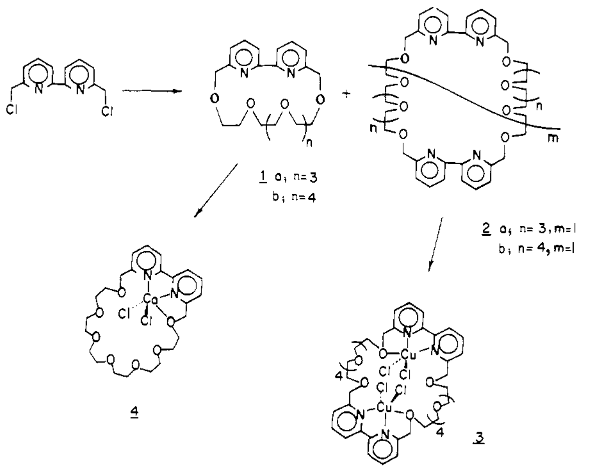
(1) Presented in part at the "Symposium on Macrocyclic Ligands", held at the Institute of Inorganic Chemistry at the University of Basel, Switzerland, July 2-4, 1980.

0002-7863/80/1502-7608$01.00/0

two-dimensional circular[2] macroligands have been studied in regard to the complexation of predominately alkali (AC) and alkaline-earth (AEC) cations;[3] however, several examples of transition-metal inclusion have been reported.[4] The incorporation of the 2,6-pyridyl moiety in the polyethereal macrocycles[5] has offered a slight advantage over simple crown ethers in AC and AEC complexation, whereas, the introduction of a 2,2′-dipyridyl subunit should facilitate binding with transition-metal ions. Although several examples of dipyridyl crown ethers have been reported,[6] most of these macrocycles are of the Schiff-base[7] or bis(lactam)[8] variety and upon complexation incorporate a single metal ion. We herein report the synthesis, complexation, and structural analysis of binuclear cation complexes of dipyridine crown ethers.



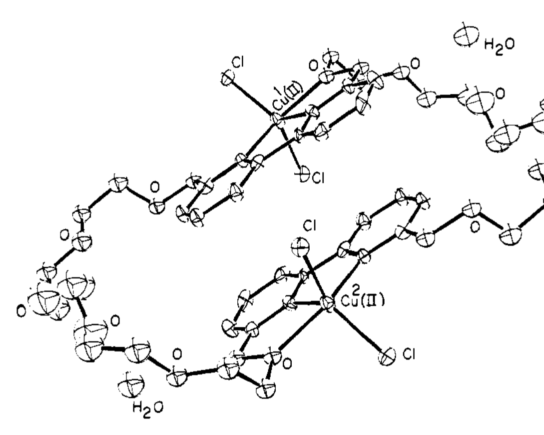


Figure 1. ORTEP plot of **3** with thermal ellipsoids shown at the 50% probability level.

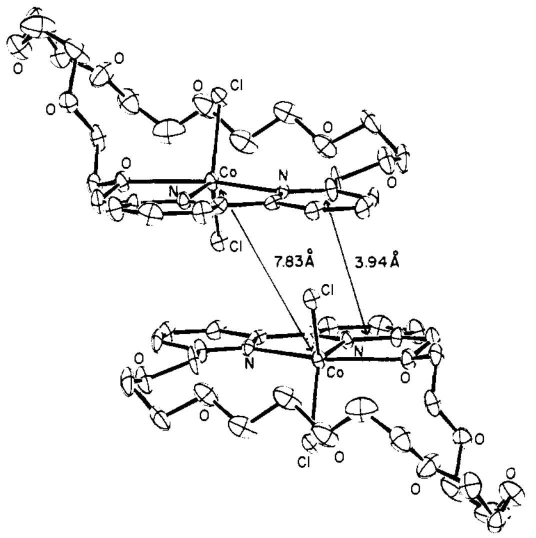


Figure 2. ORTEP plot of **4** within the crystal lattice with thermal ellipsoids shown at the 50% probability level.

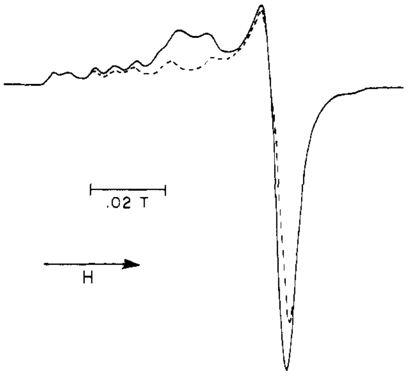


Figure 3. ESR spectrum (solid lines) of **3** in methanol at 77 K. Concentration 10^{-3} M, modulation amplitude $2.0 \times 10^{-4} T$, microwave power 1 mW, microwave frequency 9.00 GHz. Dashed lines represent the computer simulated spectrum from two noninteracting Cu(II) ions of equal concentration in different environments (see text). Broadening observed in the empirical spectrum could be due to exchange interaction.

We recently described the synthesis of a 1:1-dipyridylhexaethylene glycol crown ether **1b**, prepared by treatment of 6,6′-bis(chloromethyl)-2,2′-dipyridine with hexaethylene glycolate.[6b] The corresponding cobalt(II) chloride complex **4** was shown by an X-ray crystal structure to form a pentacoordinate complex containing a Co(II)–O (ether) bond. As side products from the ligand synthesis, the 2:2- or 3:3-macroligands (**2** (m = 1 and 2, respectively)) were also isolated. When **1b** [oil; 11%; NMR ($CDCl_3$, 200 MHz) δ 3.68, 3.78 (2s, CH_2O, 24 H), 4.80 (s, py-CH_2O, 4 H), 7.58 (dd, 5-py-H, $J_{4,5}$ = 7.8 Hz, $J_{3,5}$ = 1.2 Hz, 2 H), 7.87 (t, 4-py-H, $J_{4,5} = J_{3,4}$ = 7.8 Hz, 2 H), 8.38 (dd, 3-py-H, $J_{3,4}$ = 7.8 Hz, $J_{3,5}$ = 1.2 Hz, 2 H); IR (neat) 1545, 1415, 1086 (COC), 765 cm^{-1}][9] was treated with 2 equiv of Cu(II) chloride in boiling absolute methanol, cooled, and allowed to stand at 25

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(2) Lehn, J. -M. *Acc. Chem. Res.* **1978**, *11*, 49.

(3) (a) *Synth. Multident. Macrocyclic Compd.* **1978**, 207–243. (b) *Prog. Macrocyclic Chem.* **1979**, 115–217. (c) Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351. (d) Christensen, J. J.; Hill, J. O.; Izatt, R. M. *Science* **1971**, *174*, 459. (e) *Struct. Bonding (Berlin)* **1973**, *16*, 1–111. (f) Newkome, G. R.; Sauer, J. D.; Roper, J. M.; Hager, D. C. *Chem. Rev.* **1977**, *77*, 513.

(4) Izatt, R. M.; Lamb, J. D.; Christensen, J. J.; Haymore, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 8344. King, R. B.; Heckley, P. R. *Ibid.* **1974**, *96*, 3118. Cassol, A.; Seminaro, A.; DeParoli, G. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1163. Bunzli, J. C. G.; Wessner, D.; Oanh, H. T. T. *Inorg. Chim. Acta* **1979**, *32*, L33. Desreux, J. F.; Duyckaerts, G. *Ibid.* **1979**, *35*, L313. de Villardi, G. C.; Charpin, P.; Coates, R.; Folcher, G.; Plurien, P.; Rigny, P.; De Rango, C. *J. Chem. Soc., Chem. Commun.* **1978**, 90.

(5) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8. Newcomb, M.; Timko, J. M.; Walba, D. M.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 6392.

(6) (a) Newkome, G. R.; Nayak, A.; Fronczek, F.; Kawato, T.; Taylor, H. C. R.; Meade, L.; Mattice, W. *J. Am. Chem. Soc.* **1979**, *101*, 4472. (b) Newkome, G. R.; Kohli, D. K.; Fronczek, F. *J. Chem. Soc., Chem. Commun.* **1980**, 9. (c) Buhleier, E.; Vögtle, F. *Liebigs Ann. Chem.* **1977**, 1080. (d) Newkome, G. R.; Hager, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 5567. (e) Rebek, J., Jr.; Trend, J. E.; Wattley, R. V.; Chakravorti, S. *Ibid.* **1979**, *101*, 4333. (f) Rebek, J., Jr.; Attley, R. V. *Ibid.* **1980**, *200*, 0000. (g) Rebek, J., Jr.; Costello, T.; Wattley, R. V. *Tetrahedron Lett.* **1980**, 2379. (h) Rebek, J., Jr.; Wattley, R. V. *J. Heterocycl. Chem.* **1980**, 17, 749.

(7) Lewis, J.; Wainwright, K. P. *J. Chem. Soc., Chem. Commun.* **1974**, 169. Hague, Z. P.; Liles, D. C.; McPartlin, M.; Tasker, P. A. *Inorg. Chim. Acta* **1977**, *23*, L21. Hague, Z. P.; McPartlin, M.; Tasker, P. A. "Abstracts of Papers", American Chemical Society–Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April, 1979; INORG 297. Bishop, M. M.; Lewis, J.; O'Donoghue, T. D.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1978**, 476. Bishop, M. M.; Lewis, J.; O'Donoghue, T. D.; Raithby, P. R.; Ramsden, J. N. *Ibid.* **1978**, 828.

(8) Buhleier, E.; Wehner, W.; Vögtle, F. *Chem. Ber.* **1978**, *111*, 200.

(9) All new compounds have acceptable analytical data.

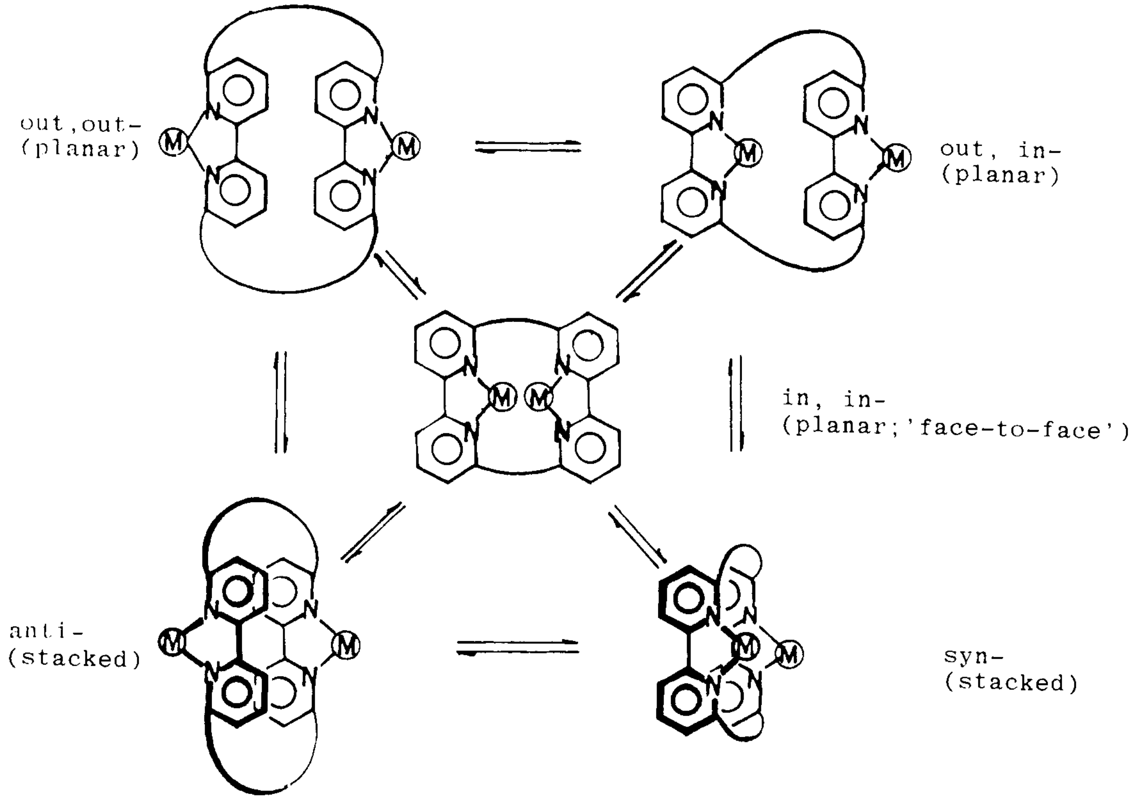

Figure 4. Nontwisted conformational extremes for the binuclear complex **3**.

°C, a yellow-green crystalline complex **3** [mp 89–90 °C; 75%; IR (KBr) 1595, 1430, 1090 cm^{-1}; UV (MeOH) λ_{max} 450 (4 × 10^3), 303 (3 × 10^4), 265 (2.4 × 10^4), and 248 (2.7 × 10^4)nm][9] was obtained.

The X-ray crystal structure of **3** was determined[10] (Figure 1). Two independent molecules exist in the unit cell, each lying on a center of symmetry. The two are quite similar, differing primarily in the conformation of the polyethereal bridges. In this binuclear complex, the Cu(II) ions are coordinated in a distorted trigonal bipyramid configuration. Bond distances within the coordination sphere average 2.319 (7) Å for Cu–Cl, 1.946 (10) Å for Cu–N equatorial, 2.049 (10) Å for Cu–N axial, and 2.123 (9) Å for Cu–O.

The conformation of **3** is shown to be such that the aromatic rings stack in a parallel fashion within a distance of 3.66 Å between ring centers and 7.16 Å between copper atoms. This situation is analogous to that observed in the intermolecular stacking of aromatic rings.[11] In the crystal structure (Figure 2) of **2a**, for instance, molecules pack such that the heteroaromatic rings of different molecules are parallel and separated (center-to-center) by 3.94 Å with a cobalt–cobalt distance of 7.83 Å. Thus, the polyethereal bridges in **3**, due to their length and flexibility, have little effect upon the packing of the complexing aromatic fragments.[12]

Obviously, it is of interest whether this crystalline structure is preserved in solution. The low-temperature (77 K) ESR spectrum of **3** in ethanol is shown in Figure 3 and can be interpreted as *arising from two dissimilar Cu(II) sites (called Cu-1 and Cu-2) of equal concentrations.* Computer simulation of each site yields the principal parameters $g_\parallel = 2.41$, $g_\perp = 2.06$, and $A_\parallel = 0.0122$ cm^{-1} for Cu-1, while $g_\parallel = 2.34$, $g_\perp = 2.06$, and $A_\parallel = 0.0149$ cm^{-1} for Cu-2. $A_\perp$ is too small to be measured for either site.

As seen in Figure 3, addition of similated spectra of each site does not completely mimic the empirical spectrum. Specifically, the broad shoulder on the low-yield side of the perpendicular region of the spectrum could be due to the close interaction of the Cu(II) ions in each molecule. This broadening is not uncommon[13] and is understandable in terms of the intramolecular Cu–Cu distance shown from the crystal data.

From inspection of the obvious possible intramolecular juxtapositions of the sites of complexation (Figure 4), only an *in-*, *out-*type conformation would best account for a near 50:50 mixture of different copper ions observed in the ESR spectrum, whereas, if the less likely intermolecular equal isomeric mixture is operative, any two of the conformational symmetrical isomers may then be possible. These data suggest that care must be exercised when a molecular cavity is defined by pictorial representations and the obvious *in*, *in* (planar) structure (derived from mononuclear complexes) can be the exception rather than the rule.

Acknowledgment. We wish to thank Dow Chemical, U.S.A., and the National Science Foundation for partial support of this work and Professor Jerry Atwood (University of Alabama) for his assistance in the acquisition of the X-ray data.

Supplementary Material Available: Coordinates of nonhydrogen atoms (Table I), temperature factors (Table II), coordinates of hydrogen atoms (Table III), and observed and calculated structure factors (Table IV) are available (17 pages). Ordering information is given on any current masthead page.

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(10) *Crystal data*: $C_{44}H_{60}N_4O_{12}(CuCl_2)_2 \cdot 2H_2O$, FW = 1141.9, space group $P\bar{1}$, $a = 12.918$ (5), $b = 12.896$ (5), $c = 18.576$ (7) Å, $\alpha = 102.08$ (3)°, $\beta = 99.12$ (3)°, $\gamma = 118.14$ (2)°, $Z = 2$, $D_C = 1.489$ g cm^{-3}, $R = 0.073$ for 2221 observed data.

(11) R. Mason *Perspect Struct. Chem.*, **1970**, *3*, 59–90.

(12) This observation is supported by the fact that the thermal parameters of atoms in the middle of the polyethereal chain are considerably larger than those of atoms near the metal atoms.

(13) Fujiwara, S.; Katsumata, S.; Seki, T. *J. Phys. Chem.* **1967**, *71*, 115.

(14) On leave from the Istituto Di Mineralogia, via San Massimo 24, 10123 Torino, Italy.

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