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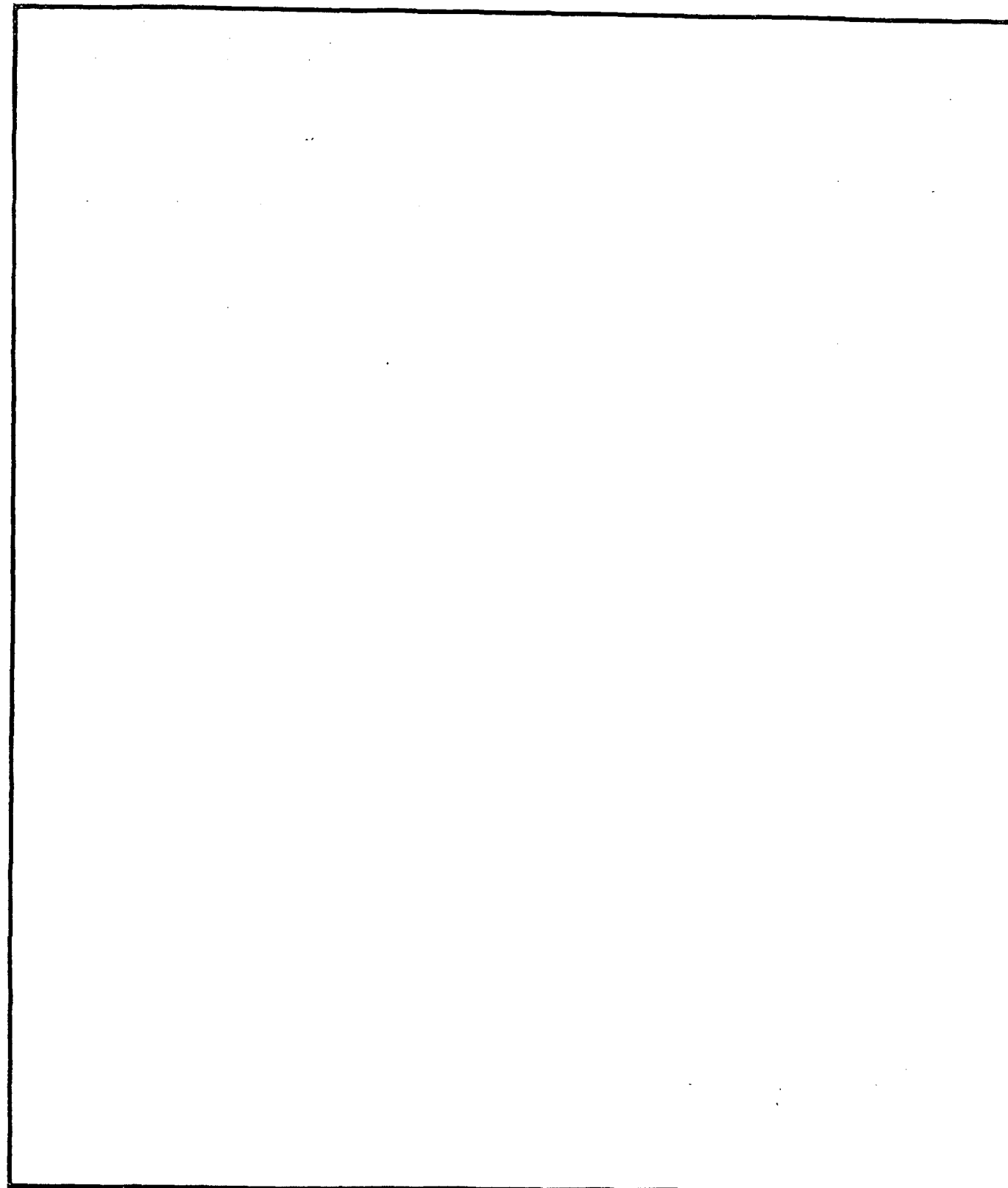
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OFFICE OF NAVAL RESEARCH

FINAL REPORT

Effective Dates: July 1, 1988 to September 30, 1991

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**Macrocyclic Polycation Complexes for Secondary Anion Binding, Molecular Recognition,
and Catalysis**

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Texas A&M Research Foundation

**Box 3578
College Station, Texas 77843**

Date submitted: February 7, 1992

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SUMMARY OF RESEARCH ACCOMPLISHED IN THIS PROJECT

A. The fourteen technical reports submitted under this research program are as follows:

Kinetics and Mechanism of the Decomposition of Cobalt Dioxygen Complexes of the Binucleating Macrocyclic Ligand BISBAMP, M. G. Basallote and A. E. Martell, *Inorg. Chem.*, **28**, 3494-3499 (1989): Technical Report No.1.

Ligand Design for Selective Complexation of Metal Ions in Aqueous Solution, R. D. Hancock and A. E. Martell, *Chem. Revs.*, **89**, 1875-1914 (1989): Technical Report No.2.

Dinuclear Complexes of a [30]Py₂N₄O₄ Macrocyclic Ligand Containing Two α,α' -Bis(amino-methyl)pyridine Moieties. Comparison with Analogous 22- and 24-Membered Macrocyclic Ligands, R. Menif, D. Chen and A. E. Martell, *Inorg. Chem.*, **28**, 4633-4639 (1989): Technical Report No.3.

Pre-organization and Molecular Recognition in the Formation and Reactions of Binuclear Metal Complexes, A. E. Martell, *Adv. Supramol. Chem.*, **1**, 145-197 (1990): Technical Report No.4.

Synthesis, Protonation, Constants, and Cu(II) and Co(II) Binding Constants of a New Octaaza Macrobicyclic Cryptand: MX₃TREN₂. Hydroxide and Carbonate Binding of the Dicopper(II) Cryptate; Crystal Structures of the Cryptand and of the Carbonato-Bridged Dinuclear Copper(II) Cryptate. R. Menif, J. Reibenspies and A. E. Martell, *Inorg. Chem.* **30**, 3446-3454 (1991): Technical Report No.5.

Template Synthesis of a Novel Macrobicyclic Ligand and the Crystal Structure of Its Unique Dinuclear Copper(I) Complex. M. P. Ngwenya, A. E. Martell and J. Reibenspies, *J. Chem. Soc. Chem. Commun.*, 1207-1208 (1990): Technical Report No.6.

Equilibrium Studies and Molecular Recognition in the Catechol- and TIRON-Bridged Binuclear Cobalt(II) 1,4,7,13,16,19-Hexaaza-10,22-dioxacyclotetracosane Dioxygen. B. Szpogancz, R. J. Motekaitis and A. E. Martell, *Inorg. Chem.* **29**, 1467-1474 (1990): Technical Report No.7.

New Hexaaza Macrocyclic Binucleating Ligands. Oxygen Insertion with a Dicopper(II) Schiff Base Macrocyclic Complex. R. Menif, A. E. Martell, P. J. Squattrito and A. Clearfield, *Inorg. Chem.* **29**, 4723-4729 (1990): Technical Report No.8.

Binding and Activation of Molecular Oxygen Within the Cavity of the Dinuclear Cobalt BISIDEN Macrocyclic Complex; Reactions with Bridging Coordination Bifunctional Reducing Substrates. A. E. Martell and R. J. Motekaitis, In: *Proc. 4th International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidation*; L. I. Simandi, Ed.; Elsevier Publishers, (1991) pp.331-336: Technical Report No.9.

A New Catalytic System for Activation of Molecular Oxygen within the Cavity of a (μ -Mesoxalato)(μ -peroxo)dicobalt-BISDIEN Complex. R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, **30**, 694-700 (1991): Technical Report No.10.

Preorganization and Molecular Recognition in Binuclear Macrocyclic and Macrobicyclic Complexes. A. E. Martell, In: *Crown Compounds, Toward Future Applications*, Ed. S. R. Cooper, VCH Publishers, in press: Technical Report No.11.

Oxygenation of a Copper(I) Complex of a Binucleating Macrocyclic Schiff Base Ligand Derived from 1,4,7-Triazaheptane and Furan-2,5-Dicarboxaldehyde. M. P. Ngwenya, D. Chen, A. E. Martell and J. Reibenspies, *Inorg. Chem.* **30**, 2732-2736 (1991): Technical Report No.12.

Molecular Recognition by O-BISDIEN and Its Dinuclear Complexes. R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, submitted: Technical Report No.13.

Molecular Recognition in the Oxidation of Catechols by Dicobalt-BISDIEN Dioxygen Complexes. F. S. Cezar, B. Szpogancz and A. E. Martell, *J. Coord. Chem.*, to be submitted: Technical Report No.14.



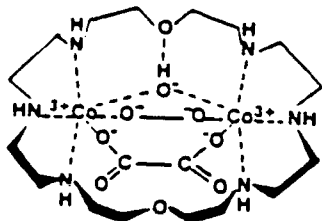
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B. Two general lines of investigation were carried out:

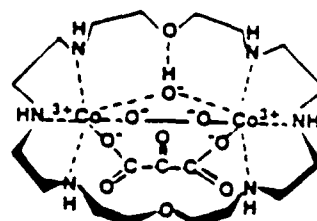
1. The activation of dioxygen through adduct formation with a dinuclear Co(II) complex of macrocyclic ligands (BISDIEN and its analogs) in which a reducing bifunctional substrate is also coordinated to both Co(II) centers.
2. The binding and activation of dioxygen through coordination with the Cu(I) centers in macrocyclic and macrobicyclic ligands.

For the Co(II)-BISDIEN systems it was previously found that a tribridged dinuclear Co(II) complex of the macrocyclic ligand BISDIEN, in which hydroxide, dioxygen (as peroxo), and oxalato anions are bound simultaneously to both metal centers, **1**, undergoes a facile redox reaction in which the dioxygen is reduced to water and the oxalate is oxidized to carbon dioxide. This work was later extended to the study of tribridged dicobalt-BISDIEN complexes containing bound dioxygen (as bridging peroxo) and bridging catecholate and disulfocatecholate as reducing substrates. The bifunctional reductants in these systems undergo two-electron oxidation, while the four-electron reduction of dioxygen to water is accomplished by conversion of the Co(II) centers to the inert dinuclear Co(III)-BISDIEN complex. This study has now been extended to catalytic systems involving four-electron reduction substrates. Thus mesoxalate (ketomalonate) is converted entirely to carbon dioxide by the loss of four electrons, while the dioxygen is reduced to water, and the metal centers remain as cobalt(II). The system **2** proved to be catalytic, and several turnovers were observed in the presence of excess mesoxalate.

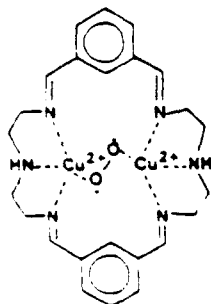
For the binuclear Cu(I) macrocyclic complexes, earlier work by this research group demonstrated that dioxygen is complexed and activated by a dinuclear Cu(I) tetra Schiff base macrocyclic ligand, resulting in oxygen insertion (hydroxylation) into a benzene ring of the macrocyclic ligand. The very reactive intermediate dioxygen complex, **3**, has too short a lifetime to be observed at room temperature. An analogous tetraSchiff base macrocyclic dinuclear Cu(I) complex with furan in place of benzene in the bridging groups does not undergo oxygen insertion, but produces a peroxo-bridged dicopper(I) complex with a measurable lifetime at and below room temperature, **4**. The use of this Cu(I) dioxygen complex for the oxidation of various substrates is now under investigation. Interestingly, a dinuclear Cu(I) complex, **5**, of a hexa Schiff base macrobicyclic (cryptand) ligand with benzene rings in the bridging groups shows no reactivity toward dioxygen or other small donor molecules, probably because of the extremely high stability of the tetracoordinated encapsulated Cu(I) ions.



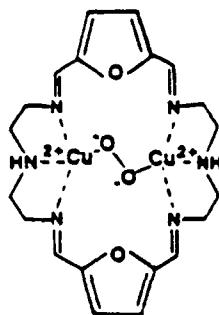
1 Oxalato-bridged BISDIEN Co₂



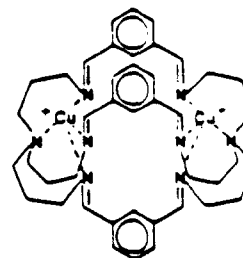
2 Mesoxalato-bridged BISDIEN Co₂



3 Reactive dinuclear Cu(I) dioxygen complex



4 Reactive dinuclear Cu(I) dioxygen complex with unreactive ligand



5 Unreactive dinuclear Cu(I) complex

C. Personnel who participated in this research.

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