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**FINAL REPORT**

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

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## SUMMARY OF RESEARCH ACCOMPLISHED IN THIS PROJECT

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

Dioxygen Activation and Transport by Dinuclear Copper(I) Macrocyclic Complexes, R. Menif, A. E. Martell, P. M. Ngwenya and D. A. Rockcliffe, in *Bioinorganic Chemistry of Copper*, Chapman & Hall, 1993 (Abstract only: *J. Inorg. Biochem.*, 47, 22, 1992): Technical Report No. 15.

The Stoichiometric and Catalytic Oxidation of Various Substrates with a Novel Macrocyclic Binuclear Cu(I) Dioxygen Complex as an Intermediate, D. A. Rockcliffe and A. E. Martell, *J. Chem. Soc., Chem. Commun.*, 1758-60 (1992): Technical Report No. 16.

Thermodynamics of Coordination of Metal Ions with Binucleating Macrocyclic and Macrobicyclic Ligands, A. E. Martell, R. J. Motekaitis, D. Chen and I. Murase, *Pure & Appld. Chem.*, 65, 959-965 (1993): Technical Report No. 17.

Oxidation Reactions of a Macrocyclic Dinuclear Copper(I) Dioxygen Complex and a Dinuclear Copper(II) Complex, D. A. Rockcliffe and A. E. Martell, *Inorg. Chem.*, 32, 3143-3152 (1993): Technical Report No. 18.

Iron(II) and Sulfate Binding by the Binucleating Ligands OBISDIEN, OBISTREN and OBISBAMP, R. J. Motekaitis, W. B. Utley and A. E. Martell, *Inorg. Chim. Acta*, 212, 15-21 (1993): Technical Report No. 19.

Molecular Recognition of Phosphite and Phosphate by the Cobalt(II)-OBISDIEN System and Oxidation of Phosphite to Phosphate by Coordinated Molecular Oxygen, R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, 33, 1032-1037 (1994): Technical Report No. 20.

Binuclear Macrocyclic and Macrobicyclic Complexes for Dioxygen Activation and Transport, A. E. Martell, R. J. Motekaitis, D. Rockcliffe, R. Menif and P. M. Nwengya, *Pure & Appld. Chem.*, 66, 859-866 (1994): Technical Report No. 21.

Equilibrium Studies of 1,2-Diaminobenzene and 3,4-Diaminobenzoate Anion with Dinuclear Cobalt(II) 1,4,7,13,16,19-Hexaaza-10,22-dioxacyclotetracosane, N. D. Rosso, B. Szpoganicz, R. J. Motekaitis and A. E. Martell, *Inorg. Chim. Acta*, 227, 49-56 (1994): Technical Report No. 22.

Oxydiacetic Acid and Copper(II) Complexes of a New Hexaaza Macrocyclic Dinucleating Ligand, A. Lobet, J. Reibenspies and A. E. Martell, *Inorg. Chem.*, 33, 5946-5951 (1994): Technical Report No. 23.

Cu(I) and Cu(II) Dinuclear Complexes of a New Hexaaza Schiff Base Dinucleating Macrocyclic Ligand and Their Oxygenation Chemistry, A. Lobet and A. E. Martell, *Inorg. Chem.*, submitted: Technical Report No. 24.

Molecular Recognition of Pyrophosphate by 1,13-Dioxa-4,7,10,16,19,22-hexaazacyclotetracosane (OBISDIEN) and by Its Mononuclear and Dinuclear Copper(II) Complexes. A Thermodynamic and Molecular Mechanics Study, P. E. Jurek, A. E. Martell, R. J. Motekaitis and R. D. Hancock, *Inorg. Chem.*, 34, 1823-1829 (1995): Technical Report No. 25.

Copper(I) and Copper(II) Dinuclear Complexes of a Macrocyclic Ligand Derived from the 2:2 Condensation of Pyridine-2,6-dicarboxaldehyde and 1,4,7-Triazaheptane, D. A. Rockcliffe and A. E. Martell, *J. Mol. Cat. A99*, 87-99 (1995): Technical Report No. 26.

Stoichiometric and Catalytic Oxidation by a Dinuclear Copper(I) Dioxygen Complex and a Dinuclear Copper(II) Complex of a Macrocyclic Ligand Derived from the 2:2 Condensation of Pyridine-2,6-dicarboxaldehyde and 1,4,7-Triazaheptane, D. A. Rockcliffe and A. E. Martell, *J. Mol. Cat.*, A99, 101-114 (1995): Technical Report No. 27

Catalytic and Stoichiometric Oxidation of Phenols and Catechols by the Dinuclear Cu(I) and Cu(II) Complexes of a Hexaaza Macrocycle Derived from the Condensation of Pyridine-2,6-dicarboxaldehyde and 1,5,9-Triazanone, D. A. Rockcliffe and A. E. Martell, *J. Mol. Cat.*, in press: Technical Report No. 28.

Molecular Recognition by the Protonated Hexaaza Macrocylic Ligand 3,6,9,16,19,22-hexaaza-27,28-dioxatricyclo[22.2.1.1<sup>11,14</sup>]-octacos-1(26),11,13,14-tetraene, Q. Lu, R. J. Motekaitis, J. J. Reibenspies and A. E. Martell, *Inorg. Chem.*, *34*, 4958-4964 (1995): Technical Report No. 29.

Molecular Recognition of Methylene-diphosphonic Acid, Methylene-diphosphonic Acid and Ethanol-1,1-diphosphonic Acid by the Dicobalt(III)-OBISDIEN System and Oxidation of These Substrates by Coordinated Molecular Oxygen, R. J. Motekaitis, I. Murase and A. E. Martell, *Inorg. Chem.*, to be submitted: Technical Report No. 30.

Copper(II) Complexes of the Hexaaza Macrocylic Ligand 3,6,9,16,19,22-hexaaza-27,28-dioxatricyclo[22.2.1.1<sup>11,14</sup>]-octacos-1(26),11,13,14-tetraene and Their Interaction with Oxalate, Malonate and Pyrophosphate Anions, Q. Lu, J. J. Reibenspies, A. E. Martell and R. J. Motekaitis, *Inorg. Chem.*, *35*, 2630-2636 (1996): Technical Report No. 31.

Studies and Molecular Recognition in the Glycylglycine, DL-Alanyl-DL-Alanine and Glycyl-L-Leucine-Cu(II)-1,4,7,13,16,19-Hexaaza-10,22-dioxacyclotetracosane Complexes, M. T. Bordignon Luiz, B. Szpoganicz, M. Rizzoto, A. E. Martell and M. G. Basalotte, *Inorg. Chim. Acta*, submitted: Technical Report No. 32.

## **B. Description of the Principal Areas of Investigation**

The main theme of this research was the study of molecular recognition of anions by macrocyclic dinucleating ligands, and by their mononuclear and dinuclear metal complexes, in addition to a study of the catalytic effects that these host-guest interactions have on guests. In some cases the guests are oxygen complexes which activate the oxygen for reaction with appropriate substrates. The reactions investigated and described in eighteen technical reports may be classified in the following four groups:

### *1. Cobalt dioxygen complexes as oxygen carriers (Technical Reports Nos. 17 and 21)*

Dinuclear Co(II) complexes of macrocyclic dinucleating ligands and dinucleating cryptands combine with dioxygen to form peroxo-bridged complexes. The dicobalt(II) OBISTREN complex is selected as the best oxygen carrier because the dioxygen complex forms and dissociates (cycles) with no appreciable degradation.

### *2. Dinuclear copper(I) dioxygen complexes (Technical Reports Nos. 16, 18, 21, 24, 26, 27, 28)*

When dinuclear copper(I) dioxygen complexes are formed so as to avoid the proximity of an aromatic -H group (which results in a rapid insertion reaction) the dioxygen complex has the unique property of being stable at room temperature and reacting as an oxidant toward phenols, catechols, hydroquinones, aromatic amines and other potentially reducing compounds. In cases where the corresponding copper(II) complex oxidizes the same substrate, a catalytic cycle may be set up for the oxidation of the substrate by oxygen with the dinuclear Cu(I)-dioxygen complex and the dinuclear Cu(II)-complex as catalysts.

3. *Recognition by macrocyclic ligands and their metal complexes (Technical Reports Nos. 17, 19, 20, 22, 23, 25, 29, 30, 31, 32)*

The protonated forms of macrocyclic dinucleating polyaza ligands, such as OBISDIEN (1,4,7,13,16,19-hexaaza-10,12-dioxacyclotetracosane) and its analogs formed by the 2+2 condensation of an aromatic dialdehyde with diethylenetriamine, recognize anions having suitable size, shape, and functional groups, and combine with them through hydrogen bond formation. The dinuclear metal complexes of these macrocyclic ligands may combine with these anions through coordinate bond formation, whereby a bi- or polyfunctional anion becomes a bridging group between the metal centers. Thus the bridging anion is the guest and the dinuclear complex of the macrocyclic ligand is the host. When a mononuclear complex of the dinucleating macrocyclic ligand is formed, the latter may be partially protonated at the uncoordinated sites, and may bind the di- or polyfunctional guest through both hydrogen bonding and coordinate bonds.

4. *The oxidation of bridging substrates by coordinated dioxygen within a dinuclear cobalt(II) OBISDIEN complex (Technical Reports Nos. 20 and 30)*

The dinuclear cobalt(II)-OBISDIEN dioxygen complex, with the oxygen present as a peroxy bridge between the metal centers, has an available (unused) coordination site on each metal, that may coordinate a bridging reducing agent. When such complexes form, raising the temperature only a little usually induces reaction of the coordinated dioxygen with the coordinated reducing agent. Thus an electron transfer occurs from the reducing guest through the metal ion to the coordinated dioxygen, all within the macrocyclic complex.

### **C. Personnel who participated in this research.**

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