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Synthesis and Characterization of Pyridine-Armed Reinforced Macrocycles and Their Transition Metal Complexes as Potential Oxidation Catalysts

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Abstract

Oxidation catalysts stable in aqueous solution under both harsh pH's and at high temperature would be environmentally friendly alternatives to current technologies. Transition metal complexes of tetraazamacrocycles reinforced with additional ethylene bridges have produced such oxidation catalysts.

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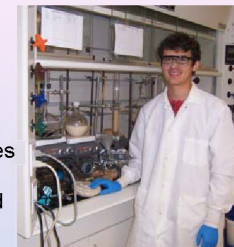


Synthesis and Characterization of Pyridine-Armed Reinforced Macrocycles and

Their Transition Metal Complexes as Potential Oxidation Catalysts

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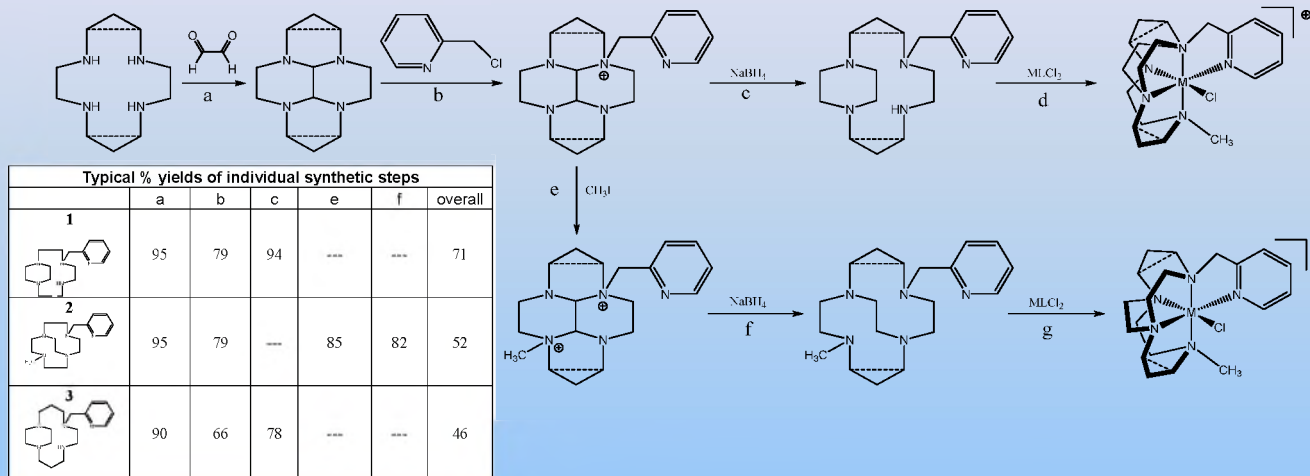


Abstract

Oxidation catalysts stable in aqueous solution under both harsh pH's and at high temperature would be environmentally friendly alternatives to current technologies. Transition metal complexes of tetraazamacrocycles reinforced with additional ethylene bridges have produced such oxidation catalysts. A controlling aspect of the usefulness of any metal catalyst is its set of oxidation and reduction potentials. Reversible redox processes that bracket a potential window within which useful oxidation of substrate molecules can occur are desirable. Though quite robust, and exhibiting reversible electrochemistry, some reinforced macrocycle complexes are not useful catalysts because their redox potentials are not in a desired potential range. An established method of modifying the electrochemical properties of a transition metal complex is to modify the ligand, which subsequently modifies the properties of its complexed metal ion. We wished to determine if the addition of pyridine pendant arms to the known reinforced macrocycle ligands would result in beneficial shifts in the redox potentials of their transition metal complexes. The resulting ligands must allow at least one open coordination site on the bound metal ion for oxidant and/or substrate binding. We have synthesized and characterized both cross-bridged and side-bridged cyclen and cyclam tetraazamacrocycles with pyridine pendant arms. Cobalt, nickel, copper, and zinc complexes were made. The synthesis and characterization of the ligands and the synthesis and characterization of their complexes will be presented.

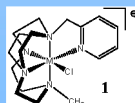
Ligand Synthesis and Transition Metal Complexation

Methods: Synthetic routes extending ethylene side-bridged and cross-bridged ligand syntheses to add pendant arms were developed. Metal complexation was performed with anhydrous solvents in an inert atmosphere glovebox to protect the proton-sponge ligands from proton and the oxygen-sensitive metal ions from oxidation.

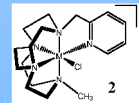


Transition Metal Complexes Synthesized

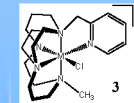
Organic Compound Elemental Analysis			
	%C	%H	%N
Picolyl Tetracyclen [C ₁₆ H ₂₄ N ₅]Cl·(4H ₂ O)			
Calc as above	48.79	8.19	17.78
Found	48.50	6.88	18.37
Side Bridged Picolyl Cyclen [C ₁₆ H ₂₇ N ₅]			
Calc as above	66.40	9.40	24.20
Found	66.15	9.61	24.20
Me-Pic-Tetracyclen [C ₁₇ H ₂₇ N ₅] ₂			
Calc as above	36.77	4.90	12.61
Found	36.79	4.69	12.69
Cross Bridged Me-Pic-Cyclen [C ₁₇ H ₂₉ N ₅] ₂ ·(0.5H ₂ O)			
Calc as above	65.35	9.68	22.41
Found	65.47	10.01	22.26
Picolyl Tetracyclam [C ₁₆ H ₂₄ N ₅] ₂ ·(0.75H ₂ O)			
Calc as above	47.53	6.54	15.40
Found	47.95	6.21	14.99
Side Bridged Picolyl Cyclam [C ₁₈ H ₃₁ N ₅] ₂ ·(1.3H ₂ O)·(0.1C ₆ H ₆)			
Calc as above	64.07	9.89	20.08
Found	63.80	10.00	19.87



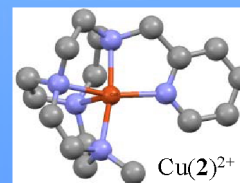
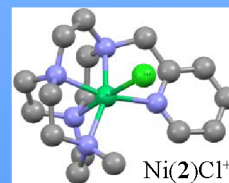
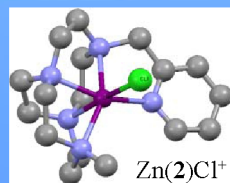
Elemental Analyses of Metal Complexes			
	%C	%H	%N
[Zn(C₁₆H₂₇N₅)](PF₆)₂			
Calc as above	29.81	4.22	10.86
Found	30.07	4.10	10.80
[Ni(C₁₆H₂₇N₅)](PF₆)₂·NH₄PF₆			
Calc as above	28.66	4.18	10.86
Found	28.43	3.79	10.75
[Co(C₁₆H₂₇N₅)]PF₆·0.5H₂O			
Calc as above	35.74	5.25	13.02
Found	35.56	5.10	12.99
[Cu(C₁₆H₂₇N₅)](PF₆)₂			
Calc as above	29.89	4.23	10.89
Found	30.37	4.07	10.70



Elemental Analyses of Metal Complexes			
	%C	%H	%N
[Cu(C₁₇H₂₉N₅)](PF₆)₂			
Calc as above	31.08	4.45	10.66
Found	30.73	4.33	10.52
[Ni(C₁₇H₂₉N₅)]PF₆·0.5H₂O			
Calc as above	37.02	5.48	12.70
Found	37.08	6.20	12.53
[Co(C₁₇H₂₉N₅)](PF₆)₂			
Calc as above	29.69	4.25	10.18
Found	29.59	4.23	10.04
[Zn(C₁₇H₂₉N₅)]PF₆			
Calc as above	37.18	5.32	12.75
Found	36.98	5.20	12.41



Elemental Analyses of Metal Complexes			
	%C	%H	%N
[Cu(C₁₈H₃₁N₅)](PF₆)₂·1.2H₂O			
Calc as above	31.22	4.86	10.11
Found	30.82	4.57	9.90
[Ni(C₁₈H₃₁N₅)]Cl₂·3H₂O			
Calc as above	43.14	7.44	13.98
Found	43.53	7.55	13.66
[Co(C₁₈H₃₁N₅)]Cl₂·0.5H₂O			
Calc as above	43.96	6.56	14.24
Found	43.99	6.91	14.17
[Zn(C₁₈H₃₁N₅)]Cl₂[ZnCl₄]			
Calc as above	36.64	5.30	11.87
Found	36.79	5.45	11.69



X-Ray Crystal Structures with Ligand 2

