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NOVEL POLYTOPIC MACROCYCLIC RECEPTOR MOLECULES CONTAINING MULTIPLE BIPYRIDYL AND DIBENZO-18-CROWN-6 UNITS

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Abstract

New polytopic macrocycles (7)-(11) containing multiple 4,4'-disubstituted-2,2'-bipyridyl and dibenzo-18-crown-6 units are described. Preliminary co-ordination studies reveal these novel ligands form polymetallic complexes with ruthenium and potassium guest cations.

Interest in transition metal polypyridyl complexes has grown rapidly in recent years due to their numerous applications in a variety of fields[1]. For example, 2, 2'-bipyridine (bpy) complexes of ruthenium[2,3], osmium[4] and rhenium[5,6] exhibit properties of importance to redox electrocatalysis and solar energy conversion[7,8]. The incorporation of multiple bipyridyl units into macrocyclic structural frameworks will lead to polynuclear transition metal complexes capable of acting as new chromophores for multielectron photoredox processes. We have recently reported a synthetic procedure for the preparation of unsymmetrical 4,4'-disubstituted-2,2'-bipyridines using step by step lithiation of 4,4'-dimethyl-2,2'-bipyridine[9]. As a continuation of this work this paper reports the syntheses and preliminary co-ordination studies of novel macrocycles containing two, three and four 4,4'-disubstituted-2,2'-bipyridyl moieties including a multisite receptor constructed of two bipyridyl and two dibenzo-18-crown-6 subunits.

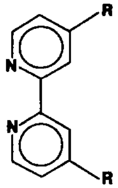
Synthèses

The new 4,4'-diformyl-2,2'-bipyridine (5) was prepared in four steps, 34% overall yield, from the commercially available starting material (1).

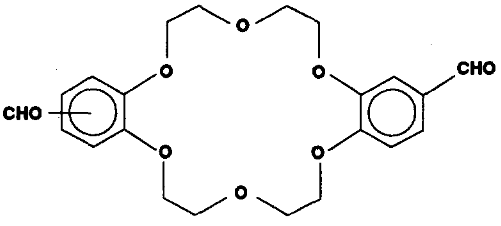
The oxidation of (1) with permanganate to give (2) has been published[10], however low and/or variable yields using the reported procedures were obtained. A highly efficient method for this conversion (90%) was achieved using chromium (VI)-oxide in sulphuric acid described by Cooper[11]. On refluxing (2) in acidic methanol the corresponding dimethyl ester (3) was isolated in 87% yield. Reduction of (3) to the diol (4) was accomplished with sodium borohydride in ethanol (72%) and oxidation to the dialdehyde (5) was achieved in 60% yield using activated MnO_2 in dioxane.

Mono-lithiation of (1) using one equivalent of lithium di-isopropylamide (LDA) in tetrahydrofuran followed by addition of 0.5 equivalent of the appropriate dialdehyde, terephthaldehyde, (5) or cis/trans isomeric mixture of dibenzo-18-crown-6 dialdehyde (6) and purification of crude products by flash chromotography on silica gave the diols (7a) (47%), (7b) (35%) and (7c) (52%) respectively.

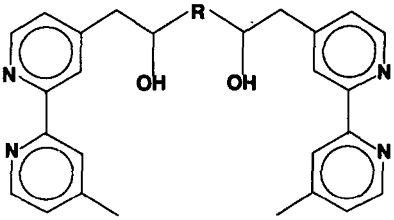
The macrocycles (8a), (8b) and (8c) were prepared in a 'one-pot' four step procedure without isolation of (7a-c) using (1) which was successively treated with one equivalent LDA, 0.5 equivalent of the appropriate dialdehyde, followed by another equivalent of LDA and 0.5 equivalent of the same dialdehyde. The crude products were sparingly soluble in common organic solvents and purification was achieved by repeated precipitation from their respective DMF-acetone or methanol solutions to give (8a) (29%), (8b) (25%) and (8c) (28%)[12].



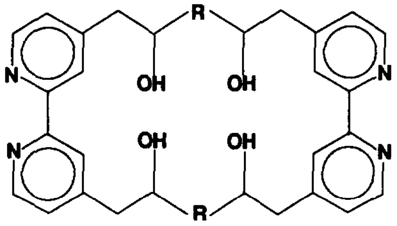
(1) R= CH_3
(2) R= CO_2H
(3) R= CO_2CH_3
(4) R= CH_2OH
(5) R= CHO



(6)



(7)



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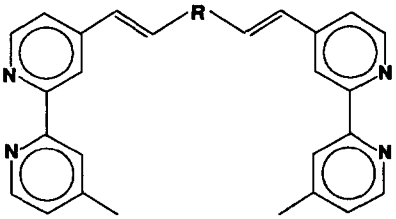
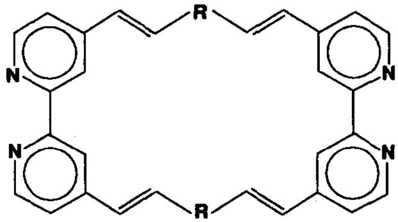


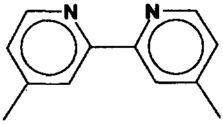
(9)



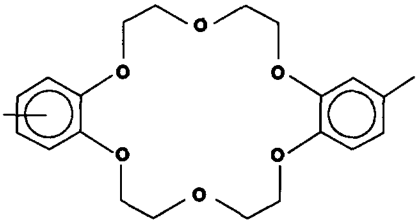
(10)

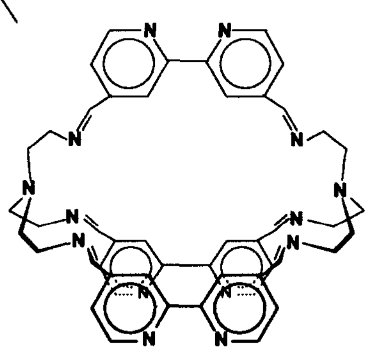
(a) R=

(b) R=



(c) R=





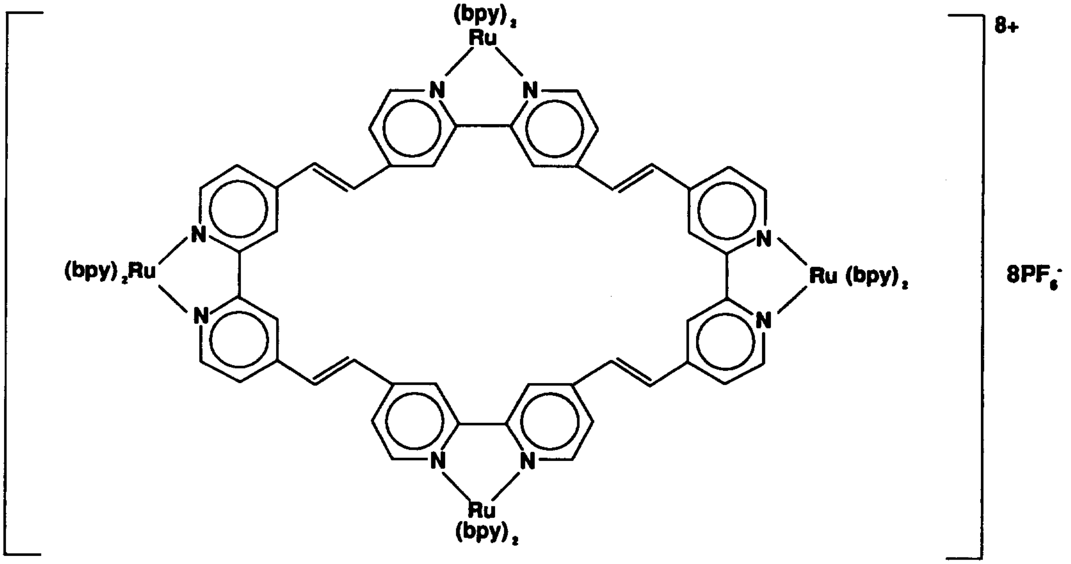
(11)

Treatment of the diols (7a-c) and the tetrols (8a-c) with phosphoric acid gave the E-isomeric alkenes (9a-c)[13] and (10a-c) in near quantitative yields.

Adapting the methodology of Lehn and co-workers[14] the novel cryptand (11) was prepared in a single step by condensing (5) (3mmol) and tris(2-aminoethyl)amine (2mmol) in dry tetrahydrofuran and isolating the precipitated white product in 75% yield.

Complexation Studies

The new macrocycles are all polytopic in design and contain multiple bipyridyl units capable of forming polymetallic transition metal complexes. Homo polymetallic ruthenium (II) complexes of (8a-c), (10a-c) and (11) were prepared by reaction of the appropriate macrocycle with an excess amount of (bpy)$_2$RuCl$_2$·2H$_2$O[15] followed by NH$_4$PF$_6$. For example with (10b) the tetrametallic complex (12) was isolated as an orange solid. The macrocycle (10c) forms a bimetallic bis ruthenium (II) complex and also binds two potassium cations, one in each of the two crown ether moieties.



(12)

The photo - and electrochemical properties of these and new hetero-polynuclear transition metal complexes are under current investigation as well as the preparation of related asymmetric macrocycles with two different bridging linkages.

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