

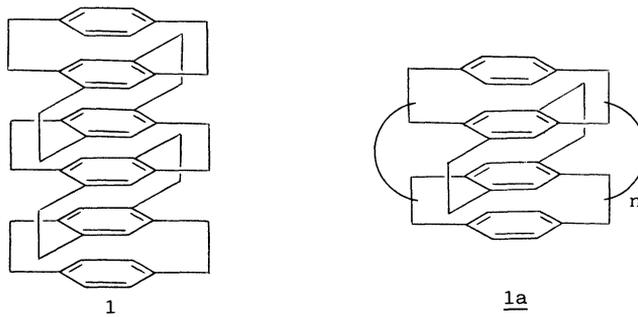
Metal complexes of $[2_n]$ cyclophanes and their mixed valence ions

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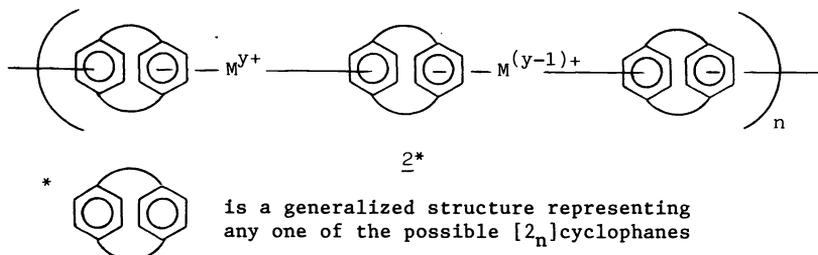
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Abstract - The possibility of synthesizing one-dimensional, π -electron delocalized, polymers of $[2_n]$ cyclophane-transition metal complexes has been explored by preparing model monomer units of selected $[2_n]$ cyclophane-ruthenium complexes and examining their properties. Bis(η^6 -hexamethylbenzene)(η^{10} - $[2_4]$ (1,2,4,5)cyclophane)diruthenium(0/II) bis(tetrafluoroborate) (14) is found to be a Class II mixed-valence compound exhibiting an unusual two-electron intervalence transfer. The discovery of $[2_n]$ -cyclophanes having three benzene decks undergoing simultaneous π -electron interaction raises the further possibility of synthesizing two-dimensional, network polymers. Tris(η^6 -hexamethylbenzene)(η^6 : η^6 : η^6 - $[2_3]$ (1,4)cyclophane-1,9,17-triene)triruthenium(II) tris(tetrafluoroborate) (19) has been prepared and the properties of its mixed-valence ions have been examined.

With the completion of syntheses of all twelve of the possible, symmetrically-bridged, $[2_n]$ -cyclophanes their physical and chemical properties, as well as their geometry, have been examined in detail (ref. 1). The outstanding characteristic of the $[2_n]$ cyclophanes, as revealed particularly from photoelectron and ESR studies (ref. 2 and 3), is the interaction of the two aromatic decks to give one overall π -electron system. This π -electron delocalization over the whole of the molecule is also observed with multilayered $[2_n]$ cyclophanes (ref. 4), as in the example of 1 having six benzene decks. Extending 1 to provide a polymer molecule (1a) having one π -electron system delocalized over a great many benzene decks would be of much interest, although at present such a synthesis appears to be prohibitively difficult.



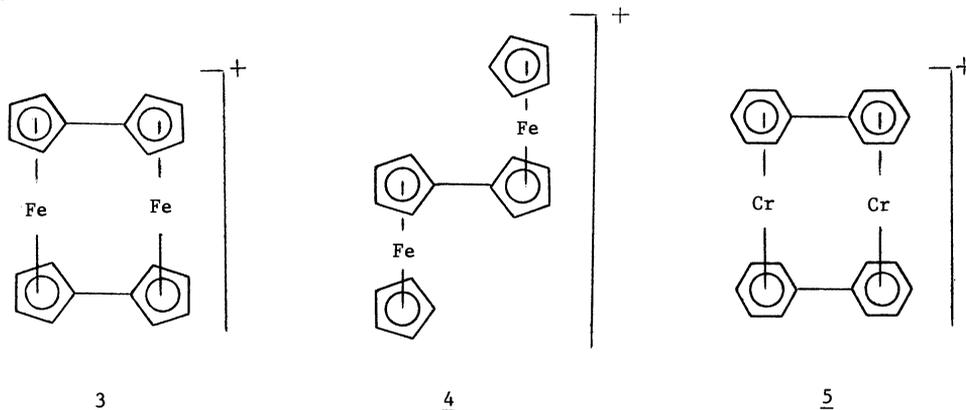
An alternate approach to a π -electron delocalized $[2_n]$ cyclophane polymer might be a polymer having monomer units of $[2_n]$ cyclophane-transition metal complexes, as shown by 2. Such



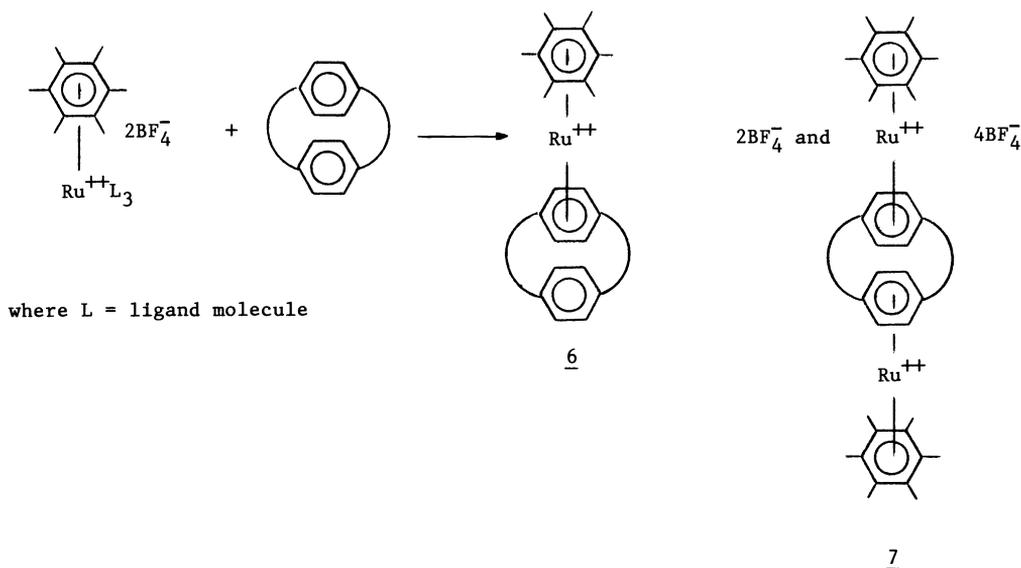
a polymer would appear to offer synthetic feasibility as well as extended π -electron delocalization. Variable valence of the transition metal atoms along the polymer chain could be of critical importance to the design of a potential electrical conductor. However, such macroscopic properties as electrical conductivity, although of practical importance, have requirements that are still ill-defined. Our concern at present, therefore, is the molecular properties of model monomer units of the type shown by 2.

The discovery of the Creutz-Taube compound (ref. 5) has spurred an enormous amount of work on electron transfer and the properties of mixed-valence ions of dimetallic complexes. These mixed-valence ions are categorized as Class I (localized metal atoms), Class II (electron interaction between metal atoms but with an energy barrier), and Class III (complete electron delocalization with the metal atoms having an average valence). For our purposes we sought Class II or, preferably, Class III behavior. The question of what combination of $[2_n]$ cyclophane with what transition metal would give a model subunit of 2 that would achieve this goal was of paramount importance. Our desired complex should have as its highest occupied molecular orbital (HOMO) a hybrid orbital with significant contributions from both the π -arene and d-metal orbitals.

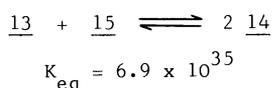
It has been shown that the bis(fulvalene)diiron ion (3) is a Class III mixed-valence ion, whereas the biferrocene ion (4) is Class II (ref. 6). Obviously, subtle, and somewhat unpredictable, factors determine the nature of the HOMO of these complexes. Another pertinent observation is that bis($\eta^6:\eta^6$ -biphenyl)dichromium ion (6) has its unpaired electron localized on chromium (ref. 7). On this basis we avoided chromium as the transition metal. Although iron seemed a possibility, we chose instead ruthenium because of its stronger bonding to arene ligands and the better synthetic methods available for preparing arene-ruthenium complexes.



Employing methods developed by Bennett for ruthenium-arene complexes (ref. 8 and 9), we prepared a series of mono- and bis-capped (η^6 -arene)ruthenium complexes of the $[2_n]$ cyclophanes, as shown in the generalized structures 6 and 7 (ref. 10).

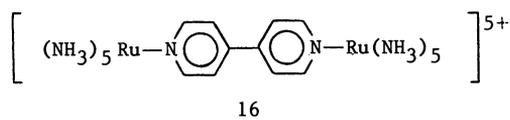


constant (6.9×10^{35}) makes it clear that solutions of 14 contain no detectable concentrations of 13 and 15.



The ¹H NMR spectrum of 14 taken in deuteroacetone at room temperature is completely symmetrical, showing singlets for the aromatic protons and methyl protons. However, when the solution is cooled, broadening of the signals occurs, then coalescence, and finally at -50°C there is a separation into two sets of signals. One set corresponds to signals observed for aromatic and methyl protons in the environment of ruthenium(II) as compared to known model compounds, whereas the other set corresponds to signals for aromatic and methyl protons in an environment of ruthenium(0) compared to related model compounds. Thus, 14 is a Class II mixed valence ion having two equivalent ground states which interconvert by a two-electron intervalence transfer.

The theory of one electron intervalence transfer for Class II mixed valence ions of the Creutz-Taube type, i.e. 16, has been developed very extensively (ref. 13). As shown



in Fig. 2, for symmetrical Class II ions involving a one-electron transfer, the thermal and optical energies required for intervalence transfer are related as $E_{\text{th}} = E_{\text{op}}/4$. For multi-electron transfers such as the two-electron transfer observed for 14, no definitive theory has yet been developed. Even so, the values for 14 of E_{thermal} , as measured from variable temperature ¹H NMR studies, and E_{optical} , as measured from the intervalence transfer band in the electronic spectrum of 14 (λ_{max} , 492 nm), bear an approximate 1:4 relationship as would be predicted from Fig. 2. Since a two-electron optical excitation is quite unlikely, some modification of these relationships from the model shown in Fig. 2 must be necessary. One possible alternative is to invoke an optically-excited $\text{Ru}^+ - \text{Ru}^+$ state as shown in Fig. 3. An attempt to portray a physical picture of the mixed-valence ion is given by 17.

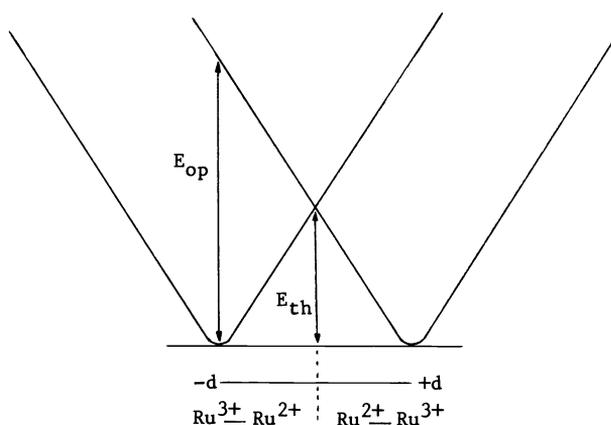


Fig. 2 Diagram of energy versus nuclear configuration for 16

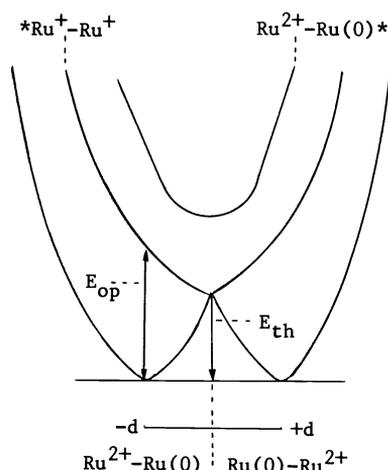
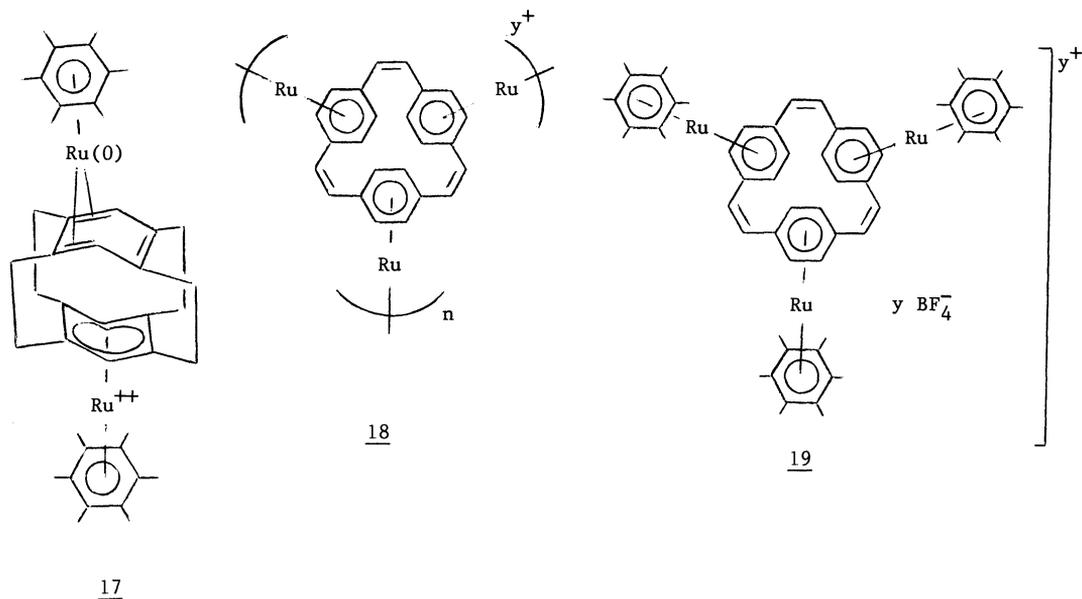


Fig. 3 Diagram of energy versus nuclear configuration for 14 (ground and excited states)

The synthesis of cyclophanes having three benzene decks undergoing simultaneous π -electron interaction has recently been reported (ref. 14). Such molecules offer the possibility of preparing two-dimensional polymers such as 18 rather than the one-dimensional polymers of the type shown by 2. It has been possible to prepare a model subunit of 18 having the tris-capped structure 19.



The behavior of 19 ($y = 6$) clearly indicates a strong π -electron interaction among the three ruthenium-capped decks. Cyclic voltammetry of 19 ($y = 6$) shows ready reduction to give ionic species of 19 where $n = 4, 3,$ and 2 . These results suggest that preparing two-dimensional polymers of the type shown by 18 may in fact be possible.

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