

Intermetallic interactions in face-to-face homo- and heterodinuclear bismacrocyclic complexes of copper(II) and nickel(II).

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Streszczenie

New face-to-face heterodinuclear complexes containing copper(II) and nickel(II) in identical tetraazamacrocyclic environments have been synthesized and characterized using ESI mass-spectrometry, X-ray diffraction, spectroscopic methods, and elemental analysis. These new bismacrocyclic systems were compared with the respective mono- and bismacrocyclic and [2]catenane homonuclear complexes. Interactions between the metal centers were monitored by magnetic and electrochemical measurements. Magnetic data indicate that all copper compounds studied behave as weakly interacting magnets. In the case of copper [2]catenane, the extent of magnetic interactions decreased when a benzocrown moiety was introduced between the macrocyclic units. On the basis of electrochemical data, the interactions between the metal centers were found to be substantially larger for the nickel complexes than for the corresponding copper ones. Interlocking of a benzocrown ether to form [2]catenane led to a nonequivalence of the metal centers and to the increase of donor abilities of the catenane compared to the respective bismacrocyclic complex. This is reflected by the shift of the first formal potential to less positive values. Intermetallic interactions for the heteronuclear nickel/copper complexes were found intermediary compared to the homonuclear ones. They were strengthened by shortening the spacer between the two tetraazamacrocyclic subunits which is a convenient way of fine-tuning the interactions. The increase of intermetallic interactions led to the increased stability of the intermediate mixed-valence states indicated by the higher values of comproportionation constants.

Słowa kluczowe

Redox reactions, Metals, Copper, Magnetic properties, Catenanes

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