Dinuclear complexes containing linear M–F–M [M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)] bridges: trends in structures, antiferromagnetic superexchange interactions, and spectroscopic properties.

Autorzy

Daniel L. Reger

Andrea E. Pascui

Mark D. Smith

Julia Jezierska

Andrew Ozarowski

Rok wydania

2012

Czasopismo

Inorganic Chemistry

Numer woluminu

51

Strony

11820-11836

DOI

10.1021/ic301757g

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The reaction of M(BF(4))(2)·xH(2)O, where M is Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II), with the new ditopic ligand m-bis[bis(3,5-dimethyl-1-pyrazolyl)methyl]benzene (L(m)*) leads to the formation of monofluoride-bridged dinuclear metallacycles of the formula [M(2)(μ-F)(μ-L(m)*)(2)](BF(4))(3). The analogous manganese(II) species, [Mn(2)(μ-F)(μ-L(m)*)(2)](ClO(4))(3), was isolated starting with Mn(ClO(4))(2)·6H(2)O using NaBF(4) as the source of the bridging fluoride. In all of these complexes, the geometry around the metal centers is trigonal bipyramidal, and the fluoride bridges are linear. The (1)H, (13)C, and (19)F NMR spectra of the zinc(II) and cadmium(II) compounds and the (113)Cd NMR of the cadmium(II) compound indicate that the metallacycles retain their structure in acetonitrile and acetone solution. The compounds with M = Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) are antiferromagnetically coupled, although the magnitude of the coupling increases dramatically with the metal as one moves to the right across the periodic table: Mn(II) (-6.7 cm(-1)) < Fe(II) (-16.3 cm(-1)) < Co(II) (-24.1 cm(-1)) < Ni(II) (-39.0 cm(-1)) ≪ Cu(II) (-322 cm(-1)). High-field EPR spectra of the copper(II) complexes were interpreted using the coupled-spin Hamiltonian with g(x) = 2.150, g(y) = 2.329, g(z) = 2.010, D = 0.173 cm(-1), and E = 0.089 cm(-1). Interpretation of the EPR spectra of the iron(II) and manganese(II) complexes required the spin Hamiltonian using the noncoupled spin operators of two metal ions. The values g(x) = 2.26, g(y) = 2.29, g(z) = 1.99, J = -16.0 cm(-1), D(1) = -9.89 cm(-1), and D(12) = -0.065 cm(-1) were obtained for the iron(II) complex and g(x) = g(y) = g(z) = 2.00, D(1) = -0.3254 cm(-1), E(1) = -0.0153, J = -6.7 cm(-1), and D(12) = 0.0302 cm(-1) were found for the manganese(II) complex. Density functional theory (DFT) calculations of the exchange integrals and the zero-field splitting on manganese(II) and iron(II) ions were performed using the hybrid B3LYP functional in association with the TZVPP basis set, resulting in reasonable agreement with experiment.

Adres publiczny

http://dx.doi.org/10.1021/ic301757g