

Hydroxide-bridged cubane complexes of nickel(II) and cadmium(II): magnetic, EPR, and unusual dynamic properties.

Autorzy

Daniel L. Reger
Andrea E. Pascui
Perry J. Pellechia
Mark D. Smith
Julia Jezierska
Andrew Ozarowski

Rok wydania

2014

Czasopismo

Inorganic Chemistry

Numer woluminu

53

Strony

4325-4339

DOI

10.1021/ic403013d

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The reactions of $M(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ ($M = \text{Ni}(\text{II})$ or $\text{Cd}(\text{II})$) and *m*-bis[bis(1-pyrazolyl)methyl]benzene (\mathbf{L}_m) in the presence of triethylamine lead to the formation of hydroxide-bridged cubane compounds of the formula $[\text{M}_4(\mu_3\text{-OH})_4(\mu\text{-L}_m)_2(\text{solvent})_4](\text{ClO}_4)_4$, where solvent = dimethylformamide, water, acetone. In the solid state the metal centers are in an octahedral coordination environment, two sites are occupied by pyrazolyl nitrogens from \mathbf{L}_m , three sites are occupied by bridging hydroxides, and one site contains a weakly coordinated solvent molecule. A series of multinuclear, two-dimensional and variable-temperature NMR experiments showed that the cadmium(II) compound in acetonitrile- d_3 has C_2 symmetry and undergoes an unusual dynamic process at higher temperatures ($\Delta G_{\text{Lm}}^\ddagger = 15.8 \pm 0.8$ kcal/mol at 25 °C) that equilibrates the pyrazolyl rings, the hydroxide hydrogens, and cadmium(II) centers. The proposed mechanism for this process combines two motions in the semirigid \mathbf{L}_m ligand termed the “Columbia Twist and Flip:” twisting of the pyrazolyl rings along the $C_{\text{pz}}\text{-}C_{\text{methine}}$ bond and 180° ring flip of the phenylene spacer along the $C_{\text{Ph}}\text{-}C_{\text{methine}}$ bond. This dynamic process was also followed using the spin saturation method, as was the exchange of the hydroxide hydrogens with the trace water present in acetonitrile- d_3 . The nickel(II) analogue, as shown by magnetic susceptibility and electron paramagnetic resonance measurements, has an $S = 4$ ground state, and the nickel(II) centers are ferromagnetically coupled with strongly nonaxial zero-field splitting parameters. Depending on the Ni–O–Ni angles two types of interactions are observed: $J_1 = 9.1$ cm⁻¹ (97.9 to 99.5°) and $J_2 = 2.1$ cm⁻¹ (from 100.3 to 101.5°). “Broken symmetry” density functional theory calculations performed on a model of the nickel(II) compound support these observations.

Adres publiczny

<http://dx.doi.org/10.1021/ic403013d>

Strona internetowa wydawcy

<https://www.acs.org/content/acs/en.html>

Plik został wygenerowany dnia 2026-04-27 10:00:02

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/gfvP9v8>.