

Ferro- vs. antiferromagnetic exchange between two Ni(II) ions in a series of Schiff base heterometallic complexes: what makes the difference?

Autorzy

Olga Yu. Vassilyeva
Elena A. Buvaylo
Vladimir N. Kozozay
Brian W. Skelton
Alexandre N. Sobolev
Alina Bieńko
Andrew Ozarowski

Rok wydania

2021

Czasopismo

Dalton Transactions

Numer woluminu

50

Strony

2841-2853

DOI

10.1039/d0dt03957h

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Three new Ni^{II}/Zn^{II} heterometallics, [NiZnL'₂(OMe)Cl]₂ (**1**), [NiZnL''(Dea)Cl]₂·2DMF (**2**) and [Ni₂(H₃L''')₂(*o*-Van)(MeOH)₂]Cl·[ZnCl₂(H₄L''')](MeOH)·2MeOH (**3**), containing three-dentate Schiff bases as well as methanol or diethanolamine (H₂Dea) or *o*-vanillin (*o*-VanH), all deprotonated, as bridging ligands were synthesized and structurally characterized. The Schiff base ligands were produced *in situ* from *o*-VanH and CH₃NH₂ (HL'), or NH₂OH (HL''), or 2-amino-2-hydroxymethylpropane-1,3-diol (H₄L'''); a zerovalent metal (Ni and Zn in **1**, Zn only in **2** and **3**) was employed as a source of metal ions. The first two complexes are dimers with a Ni₂Zn₂O₆ central core, while the third compound is a novel heterometallic cocrystal salt solvate built of a neutral zwitterionic Zn^{II} Schiff base complex and of ionic salt containing dinuclear Ni^{II} complex cations. The crystal structures contain either centrosymmetric (**1** and **2**) or non-symmetric di-nickel fragment (**3**) with Ni⋯Ni distances in the range 3.146–3.33 Å. The exchange coupling is antiferromagnetic for **1**, $J = 7.7 \text{ cm}^{-1}$, and ferromagnetic for **2**, $J = -6.5 \text{ cm}^{-1}$ (using the exchange Hamiltonian in a form $\hat{H} = J\hat{S}_1\hat{S}_2$). The exchange interactions in **1** and **2** are comparable to the zero-field splitting (ZFS). High-field EPR revealed moderate magnetic anisotropy of opposite signs: $D = 2.27 \text{ cm}^{-1}$, $E = 0.243 \text{ cm}^{-1}$ (**1**) and $D = -4.491 \text{ cm}^{-1}$, $E = -0.684 \text{ cm}^{-1}$ (**2**). Compound **3** stands alone with very weak ferromagnetism ($J = -0.6 \text{ cm}^{-1}$) and much stronger magnetic anisotropy with $D = -11.398 \text{ cm}^{-1}$ and $E = -1.151 \text{ cm}^{-1}$. Attempts to calculate theoretically the exchange coupling (using the DFT “broken symmetry” method) and ZFS parameters (with the *ab initio* CASSCF method) were successful in predicting the trends of J and D among the three complexes, while the quantitative results were less good for **1** and **3**.

Adres publiczny

<http://dx.doi.org/10.1039/d0dt03957h>

Strona internetowa wydawcy

<https://www.rsc.org/>

Plik został wygenerowany dnia 2026-05-06 03:22:07

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/vJNvg80>.