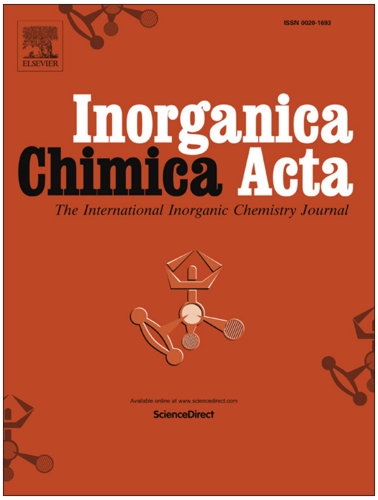

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Dominik Lomjanský, Cyril Rajnák, Ján Titiš, Ján Moncoľ, Lukáš Smolko, Roman Boča

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Impact of tetrahedral and square planar geometry of Ni(II) complexes with (pseudo)halide ligands to magnetic properties

Dominik Lomjanský[a], Cyril Rajnák[a*], Ján Titiš[a*], Ján Moncoľ[b], Lukáš Smolko[c], and Roman Boča[a]

[a] *Department of Chemistry, Faculty of Natural Sciences, University of SS Cyril and Methodius, 917 01 Trnava, Slovakia, cyril.rajnak@ucm.sk, jan.titis@ucm.sk*
[b] *Institute of Inorganic Chemistry, Slovak University of Technology, 812 37 Bratislava, Slovakia*
[c] *Faculty of Medicine, J.P. Šafárik University in Košice, Košice, Slovakia*

Abstract

Four tetracoordinate Ni(II) complexes have been prepared, structurally characterized, and subjected to magnetometric studies. The complexes [Ni(PPh$_3$)$_2$(NCS)$_2$], [Ni(*dppp*)(NCS)$_2$], and [Ni(*dppm*)Br$_2$] are planar and thus diamagnetic. The complex [Ni(*biqu*)Br$_2$] is quasi-tetrahedral, with the geometry close to C_{2v} symmetry, and paramagnetic. While on one side it resembles a prolate bisphenoid (the angle N-Ni-N = 83 deg), on the second side it mimics an oblate bisphenoid (Br-Ni-Br = 126 deg). It exhibits a zero-field splitting of the ground term $^3A_2$ into three crystal-field multiplets that can be described by D and E parameters within the spin Hamiltonian formalism. The *ab initio* calculations confirm this interpretation; however, the evaluation of the spin-Hamiltonian parameters meets difficulties owing to the quasi-degeneracy of the electronic terms.

Key words
Ni(II) complexes, P-donor ligands, N-donor ligands, (pseudo)halide ligands, paramagnetism, diamagnetism.

1. Introduction

Magnetic anisotropy of transition metal complexes attracts much attention in the recent period because this is a key factor that induces the slow magnetic relaxation and consequently a behavior of the metal complexes as single molecule (single ion) magnets – SMMs, SIMs. The SIM behavior has been observed among several first-row transition metal complexes such as V(IV), Cr(III), low-spin Mn(IV), Mn(III), Fe(III), Fe(II), Fe(I), Co(II), Ni(II), Ni(I), and Cu(II) [1-11]. Though some families are extremely rich, such as tri-, tetra-, penta-, hexa-, hepta- and octacoordinate Co(II) complexes, some are represented only by a few or a single example [12, 13]. The class of Ni(II) SIMs is limited only to three compounds so far of which [Ni(*pydca*)(*dmpy*)]·H$_2$O and [Ni(NCS)$_2$(*nqu*)$_2$(H$_2$O)$_2$]·2*nqu* are hexacoordinate, and [Ni(*mdabco*)$_2$Cl$_3$]ClO$_4$ is pentacoordinate [14, 15]. All of them possess negative axial zero-field splitting parameter $D < 0$ (-13.7, -5.9, and -311 cm^{-1}) as a prerequisite of the barrier to spin reversal that facilitates the SIM behavior. The class of hexacoordinate Ni(II) complexes is a widely studied and well understood case where the magnetic anisotropy parameter can be predicted and tuned on the basis of the magnetostructural D-correlation [16].

The class of tetracoordinate Ni(II) complexes is studied in a lower extent. There is one obstacle: owing to the Jahn-Teller effect the ground electronic term $^3T_1$ in the tetrahedral geometry is unstable and the geometry is stabilized along the e-mode of distortion leading either to the $^3A_2$ or ^3E state of the D_{2d} geometry. The latter is also unstable and the distortion continues to the stable geometry of the C_{2v} symmetry (or lower) with $^3A_1$, $^3B_1$, $^3B_2$ terms. Another obstacle originates in weaker crystal-field strength of the tetrahedral systems when compared to the octahedral ones: the quasi-degeneracy is a common feature since the energy gap Δ_{ax} between the ground and the first excited terms is rather low. This causes that the evaluation of the traditional spin-Hamiltonian parameters (D and E) could violate because the perturbation theory tends to diverge.