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Trinuclear Nickel(II) Complex through a 2,3,5,6-Tetrakis(2-pyridyl)pyrazine Ligand with a Linear Exchange Pathway

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The compound $[Ni_3(tppz)_2(NCS)_2(H_2O)_4](NO_3)_4 \cdot 4H_2O$ [tppz = 2,3,5,6-tetrakis(2-pyridyl)pyrazine and NCS = thiocyanate ligand] consists of trimeric units, where the three Ni^{II} cations are linked by two bis-tridentate tppz ligands. This compound crystallizes in the monoclinic space group $C2/c$, with $Z = 4$, $a = 25.1116(12)$ Å, $b = 10.8127(5)$ Å, $c = 25.2294(13)$ Å, and $\beta = 116.856(5)°$. The crystal structure is in good agreement with the antiferromagnetic interactions because of unidirectional coupling through the tppz ligands.

Over the last years, enormous efforts have been made in the synthesis of new high-dimensional coordination polymers on the basis of concepts such as crystal engineering, molecular architecture, etc.[1] For the preparation of these systems, the selection of the appropriate ligands is relevant. The pseudohalide ligands have been demonstrated to be not only extremely versatile but also excellent magnetic couplers.

On the other hand, polyazine-based heterocyclic bridging ligands capable of mediating intermetallic electronic communications through the π-symmetry orbitals have been investigated[2] since the discovery of the pyrazine-mediated strong intermetallic coupling in the Creutz−Taube complex.[3] In this sense, 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz) has been found to be a suitable mediator for intermetallic coupling almost on the order of the Creutz−Taube ion.[2h−k,n,q−t]

The coordination modes of the tppz ligand are bidentate,[4] tridentate,[2k,5] bis-bidentate,[4a,6] tris-bidentate,[4a] and bis-tridentate.[5e,7]

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Attempts focused on the complex formation between tppz, pseudohalide ligands, and first-row transition-metal ions showed different results.[5e,8] It seems that the nuclearity of the product depends on the choice of anions and the reaction conditions.[9]

Note that metallorganic units of this ligand with transition-metal ions are used as linkers to generate systems of high-dimensionality.[10]

More recently, structural, spectroscopic, and magnetic studies on a tppz-bridged metal complex have been reported.[5e,g,h,11]

In this Communication, we present the synthesis, spectroscopy, crystal structure, and magnetic characterization of the trimer $[Ni_3(tppz)_2(NCS)_2(H_2O)_4]\ (NO_3)_4 \cdot 4H_2O$ (**1**).

The crystal structure[12] of **1** consists of trinuclear units, where the three Ni^{II} cations are linked by two bis-tridentate tppz ligands. Because of this coordination mode, tppz displays a strong distortion concerning the planarity of the pyridine groups. In this sense, the central pyrazine ring shows torsion angles N2−C11−C12−N5 = 21.5(4)° and N2−C13−C14−N5 = 22.8(4)°. This compound exhibits two crystallographically independent metallic centers that are octahedrally coordinated. The central nickel atom Ni1 is connected to two tppz ligands, in a meridional conformation, through six Ni−N(tppz) bonds. The atom Ni2 and its equivalent by symmetry are linked to one tppz by three Ni−N(tppz) bonds in the equatorial position. In this case, the octahedral coordination sphere is completed by binding to the nitrogen atom of the NCS group and to two oxygen atoms of the coordinating water molecules (Figure 1). Furthermore, each trimer unit contains four nitrate anions to stabilize the charge of the cationic unit and four crystallization water molecules.

The trimeric units are packed along the [010] direction, showing groups of trimers that pack alternately in the *xz* plane (Figure 2). The crystallization water molecules and the nitrate anions are in the hollows of the structure.

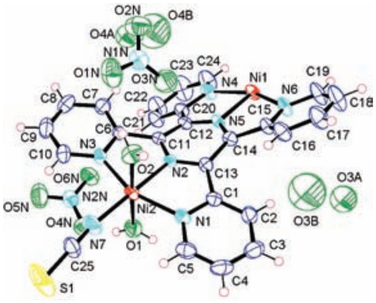

Figure 1. ORTEP view of the asymmetric unit, with atom labeling, for compound **1**. The disorder of the solvation water molecules originates splitting in the positions of their oxygen atoms.

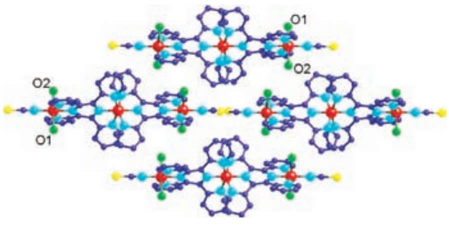

Figure 2. Arrangement of the trimers in the [010] direction. The relative orientation of the oxygen atoms of the coordinating water molecules is shown.

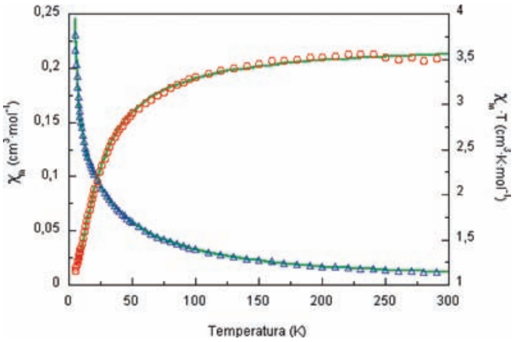

Figure 3. Thermal dependence of $\chi_m T$ and χ_m.

The thermal evolution of the magnetic molar susceptibility is shown in Figure 3 in the form of $\chi_m T$ and χ_m vs temperature plots. The room temperature $\chi_m T$ value ($3.5\ cm^3 \cdot K \cdot mol^{-1}$) agrees well with that expected for three noninteracting single-ion triplet states.[13] Upon cooling, the magnetic effective moment decreases slowly from 300 K and more quickly below 50 K, being $\chi_m T = 1.16\ cm^3 \cdot K \cdot mol^{-1}$ at 5 K. On the other hand, the reciprocal susceptibility follows the Curie−Weiss law down to 50 K, with values of C_m and θ of $3.69\ cm^3 \cdot K \cdot mol^{-1}$ and −11.9 K, respectively. Both the negative temperature intercept and the continuous decrease of the magnetic effective moment with decreasing temperature indicate the presence of antiferromagnetic interactions in this trinuclear compound.

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(12) Crystal data for **1**: crystal dimens 0.09 × 0.07 × 0.03 mm, monoclinic, *C2/c*; $a = 25.1116(12)$ Å, $b = 10.812(5)$ Å, $c = 25.2294(13)$ Å, $\beta = 116.856(5)°$, $V = 6111.5(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.579\ g \cdot cm^3$, $\theta_{max} = 32°$, $\theta_{min} = 3.1°$, Oxford Diffraction Xcalibur 2 diffractometer, $T = 293(2)$ K, λ(Mo Kα) = 0.710 73, $\mu = 1.072\ mm^{-1}$, 30 948 reflections, 9734 unique reflections, 419 parameters, R1 = 0.0620 [$I > 2\sigma(I)$], wR2 = 0.1529, maximum residual electron density 0.59 e·Å^{-3}.

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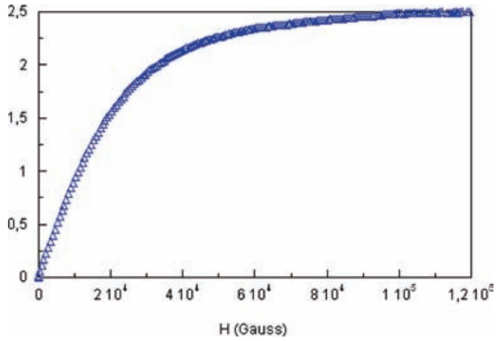


Figure 4. Magnetization versus applied field at 2 K.

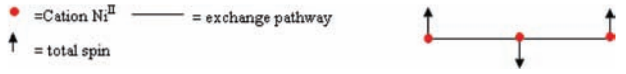


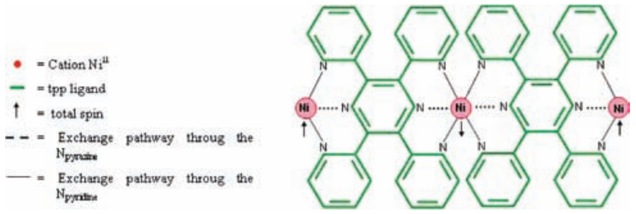
Figure 5. Antiferromagnetic interactions in the linear nickel trimer.

Moreover, the magnetization versus applied field curve, registered at 2 K (Figure 4), shows saturation with a $M/N\beta$ value close to 2.5. This is typical for antiferromagnetically coupled high-spin Ni_3 systems with $S = 1$ (Figure 5) and allows us to discard the Ni^{II} single-ion zero-field splitting as the origin of the observed magnetic behavior.

The magnetic exchange interactions of centrosymmetric trimers with $S = 1$ are usually described by the isotropic Hamiltonian $H = -2J[(S_1 \cdot S_2) + (S_2 \cdot S_3)] - 2J_{13}(S_1 \cdot S_3)$, where J and J_{13} represent the exchange coupling constants between neighboring and terminal ions, respectively. In the absence of a clear exchange pathway between terminal ions, J_{13} is taken as zero.[13b,c] Application of van Vleck's susceptibility equation and the addition of the Zeeman term to the precedent Hamiltonian (considering equal and isotropic g values for the three nickel ions) give the following expression for the molar susceptibility:

$$\chi = \frac{2Ng^2\beta^2}{3\kappa T}\,\frac{3+42e^{4x}+15e^{2x}+18e^{-2x}+3e^{-6x}}{3+7e^{4x}+5e^{2x}+8e^{-2x}+e^{-4x}+3e^{-6x}} \quad (1)$$

Scheme 1. Scheme for Unidirectional Antiferromagnetic Coupling



N stands for Avogadro's number, g the Landé factor, β the Bohr magneton, and k the Boltzmann's constant, and $x = J/kT$. The best least-squares fit (solid line in Figure 3a) was obtained for the following values: $J/k = -6.2$ K and $g = 2.22$. This low exchange constant is consistent with the absence of the expected plateau characteristic of a $S = 1$ system resulting from an antiferromagnetically coupled trinuclear Ni^{II} complex. Moreover, it agrees well with the large intermetallic distance through the pyrazine group of tppz (6.69 Å), which is shorter than the distance involving the pyridyne group [11.27(8) Å][14] and therefore must be considered as the main exchange pathway (Scheme 1) for this compound.

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Supporting Information Available: Detailed experimental procedures, figures depicting the structure, IR and UV–vis spectroscopies, thermal behavior, and a X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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