A novel ferromagnetically-coupled trinuclear nickel(II) complex constructed from the new 1,2-di(pyridin-2-yl)ethanone ligand in its enolate form

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ABSTRACT

Solvothermal reaction of $Ni(OAc)_2$ with the new ligand 1,2-di(pyridin-2-yl)ethanone (H**L**) in the presence of NH_4SCN in DMF/CH_3OH solution affords a novel trinuclear Ni^{2+} complex $[Ni_3(L)_2(OAc)_2(SCN)_2(DMF)_2](DMF)_{1.5}(H_2O)$ (**1**). Crystal structure determination of **1** reveals a non-collinear Ni_3-pattern bridged by the μ_2-$O_{enolate}$ atoms of **L**⁻ and μ_3-acetate anions, which has rarely been found for trinuclear Ni^{2+} systems. Moderate ferromagnetic exchange was observed between the Ni^{2+} centers.

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Over the past decades, polynuclear coordination assemblies constructed using crystal engineering strategy are of special interests, not only owing to their diverse structural architectures, but also to their potential applications in magnetochemistry, catalysis and biological aspects [1–5]. As a reliable synthetic methodology, the proper selection of organic linkers, which can bridge the metal centers in different manners, will play a pivotal role in design and preparation of such metallosupramolecular systems [6]. In this connection, polypyridyl ketone ligands such as di-2-pyridyl ketone [7] and 2,6-bis(2-pyridylcarbonyl)pyridine [8], which normally undergo the metal-assisted alcoholysis to afford the hemiacetal derivatives, have been widely applied to synthesize a variety of polynuclear metal complexes, from simple dinuclear species to elegant icosanuclear aggregate.

Recently, the analogous dipyridyl ketone ligands with unsymmetric skeletons, for example, 2-hydroxy-[1,2-di(pyridin-2-yl)]ethane-1-one [9], 2-pyridinyl-4-pyridinylmethanone [10] and 2-pyridinyl-3-pyridinyl-methanone [11], attract increasing attention due to their distinct linking roles in coordination assemblies, which are quite sensitive to metal centers, anions and solvents. In the present work, we have synthesized a new extended analogue of di-2-pyridyl ketone, i.e. 1,2-di(pyridin-2-yl)ethanone (H**L**), in which one methylene is introduced between the carbonyl and one terminal 2-pyridyl [12]. The ¹H NMR spectrum of H**L** (see Fig. S1) clearly reveals the typical keto-enol tautomerism, namely the co-existence of both enolate and ketone

formats (see Scheme 1) with an approximate 3/1 molar ratio. As a result of the reaction of H**L** with nickel acetate, a novel trinuclear Ni^{2+} complex $[Ni_3(L)_2(OAc)_2(SCN)_2(DMF)_2](DMF)_{1.5}(H_2O)$ (**1**) with the deprotonated enolate-type **L**⁻ ligand can be obtained, where the three non-collinear octahedral Ni^{2+} centers are linked by both O-enolate and acetate bridges to result in moderate ferromagnetic interactions.

Solvothermal reaction of $Ni(OAc)_2$, H**L** and NH_4SCN with a 4/1/1 ratio in DMF/methanol at 100 °C for 3 days affords a clear solution, which will yield the single crystals of **1** upon slow solvent evaporation [13]. The composition of **1** was characterized by elemental analysis and IR spectrum. Notably, **1** can only be obtained under solvothermal conditions and the conventional solution assembly will produce no solid product. Additionally, a higher metal-to-ligand ratio is generally required to afford such polynuclear systems [8c] and the presence of thiocyanate and acetate will also account for the formation of the final crystalline product.

Single crystal X-ray diffraction analysis [14] indicates that **1** consists of a neutral trinuclear Ni^{2+} unit and lattice DMF/H_2O solvents. As shown in Fig. 1, the three independent Ni^{2+} ions take an isosceles triangular arrangement and are bridged by two deprotonated enolate-type **L**⁻ ligands and a pair of acetate anions. Ni1 is six-coordinated to two pyridyl nitrogen donors, two enolate oxygen atoms from different **L**⁻ ligands and two carboxylate oxygen atoms of acetates, showing a distorted octahedral coordination sphere. Ni2 and Ni3 centers exhibit similar coordination geometry, that is, each octahedral metal ion is surrounded by two nitrogen donors from pyridyl and one terminal SCN⁻ anion as well as four oxygen atoms from two acetates, one enolate group of **L**⁻ ligand and one DMF solvent. The average bond distances of Ni–N and Ni–O are 2.037 and 2.079 Å, being consistent with those reported for other similar Ni^{2+} complexes [7c].

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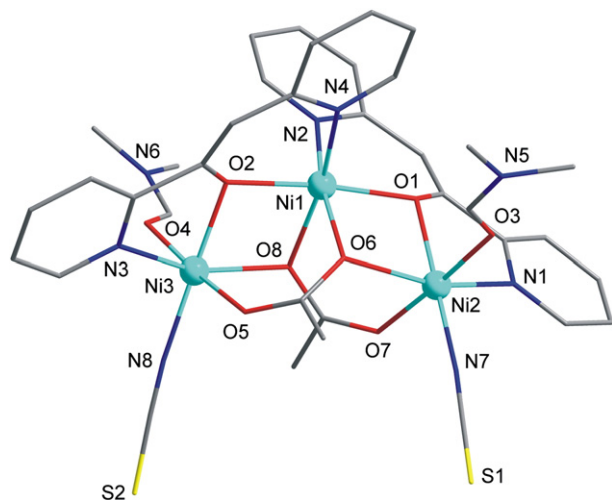   *E-mail addresses:* dumiao@public.tpt.tj.cn (M. Du), albert.escuer@ub.edu (A. Escuer).
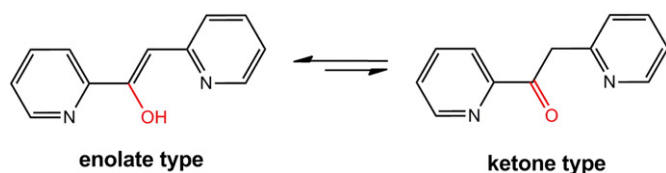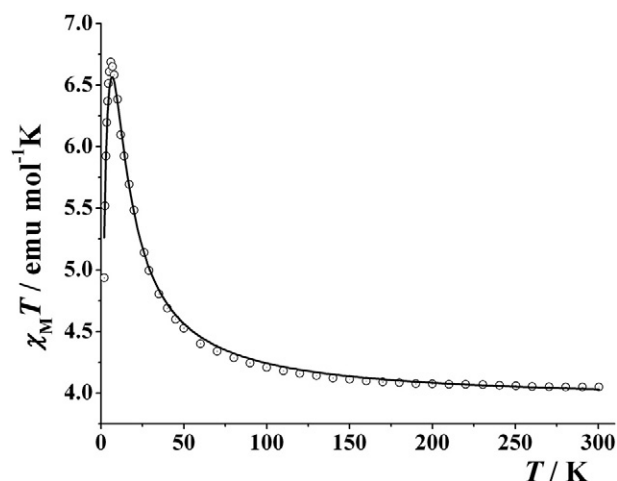
Scheme 1. Keto-enol tautomerism of the ligand H**L**.

Each deprotonated enolate ligand **L**$^-$ is coordinated to two Ni^{2+} centers in μ_2-η^1:η^2:η^1 mode to form a dinuclear unit and two such dimeric units sharing the Ni1 center are further combined to constitute the final trinuclear motif, with the aid of two additional μ_3-η^1:η^2 acetate anions. In this case, the SCN$^-$ anions and DMF solvents only act as the terminal ligands. The distances between Ni1···Ni2 and Ni1···Ni3 are 3.101 and 3.100 Å and that of Ni2···Ni3 is 4.938 Å. Notably, a Cambridge Structural Database (CSD) search suggests only 12 hits for such a trinuclear pattern with both μ_2-OR and μ_3-acetate bridges, among which 8 cases are Ni^{2+} systems [15] and the others are Co^{2+} and Mn^{2+} species [15,16c]. Moreover, all of these examples are synthesized by the phenol-based Schiff bases and in this sense, the ligand **L**$^-$ in **1** represents a new type of tecton for constructing such trinuclear motifs. Besides, due to the conjugated enolate-skeleton of **L**$^-$, the ligands show the rigid features with a nearly planar structure, where the dihedral angles of two terminal pyridyl rings are 6.9/1.8° and the N1–C5–C6–O1/N3–C17–C18–O2 torsion angles are 8.5/11.8°. Each ligand affords one 5- and one 6-membered chelating rings with Ni2/Ni3 and Ni1 ions in the trinuclear unit.

Further analysis of the crystal packing reveals that the trinuclear motifs are well isolated in the 3-D crystalline lattice, in which no significant secondary interaction is observed. Along the [100] direction, it can be clearly viewed that a solvent-layer of H$_2$O/DMF is formed, by which two adjacent layers composed by the trinuclear units are separated (see Fig. S2). A calculation of the guest-accessible-area [17] shows the values of 76.2 and 692.6 Å^3 before and after removing the lattice H$_2$O/DMF solvents, corresponding to 3.0% and 27.2% per unit cell volume.

Room temperature $\chi_M T$ value for complex **1** is 4.05 cm^3·mol^{-1}·K, which is larger than the expected value for three isolated $S = 1$ spins (3.00 cm^3·mol^{-1}·K for $g = 2.00$). On cooling, the $\chi_M T$ value increases continuously up to the maximum value of 6.68 cm^3·mol^{-1}·K at 6 K. Below this temperature, a slight decrease of $\chi_M T$ down to 4.93 cm^3·mol^{-1}·K at 2 K occurs (see Fig. 2). The χ_M vs. T plot shows a continuous increase on cooling in the whole temperature range. The room temperature value and the continuous increase of


Fig. 2. Plot of the $\chi_M T$ product vs. T for complex **1**. The solid line shows the best fit of the experimental data (see text for details).

$\chi_M T$ up to the expected value for an $S = 3$ ground state suggest the presence of a dominant ferromagnetic interaction in **1**.

Structural data of **1** show double O-enolate bridges with similar bond parameters plus one *syn-syn* acetate bridge between Ni1···Ni2 and Ni1···Ni3 and double *syn-anti* acetate bridges between Ni2···Ni3 (see Scheme 2). Accordingly, analysis of the magnetic data was performed by the expression for an isosceles triangle derived from the following Hamiltonian [18]:

$$H = -J_1(S_1 \cdot S_2 + S_1 \cdot S_3) - J_2(S_2 \cdot S_3).$$

The best fit parameters were obtained as $J_1 = J_2 = +4.6(1)$ cm^{-1} and $g = 2.288(3)$. Low T decay was corrected by means of a Weiss parameter of $\theta = -0.98$ K. The similar values found for both coupling constants are clearly a mathematic artifact, which should be assumed as a mean value because comparable results can also be obtained (for example: $J_1 = +5.6(2)$ and $J_2 = +3.0$ cm^{-1}) when fixing J_2 at lower values. On the other hand, simulations by fixing a negative value for J_2 give unacceptable fits discarding its negative sign. The conclusion is that **1** shows a moderate ferromagnetic response with positive values for both coupling constants. Such results agree well with the structural data: the double Ni–O–Ni bridges have values of ca. 92.0° for the acetate oxygen and ca. 102.2° for enolate oxygen, giving a mean value compatible with ferromagnetic interactions. In addition, the interactions promoted by *syn-anti* acetate bridges are normally weak and ferromagnetic in nature [19]. Here, the presence of *syn-syn* acetate for J_1 pathway will lead to antiferromagnetic coupling

Fig. 1. The trinuclear coordination unit of **1**.
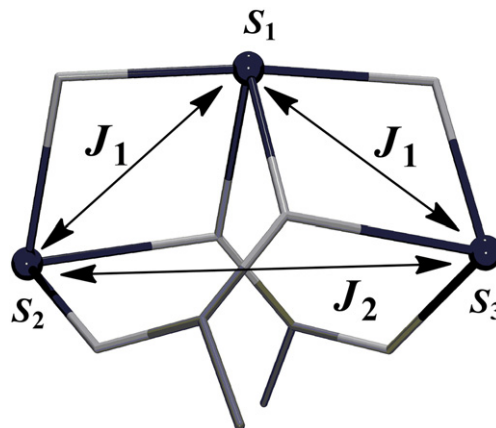
Scheme 2. Magnetic interactions in complex **1**.