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Communication

Ferromagnetism in a Dinuclear Nickel(II) Complex Containing Triethylenetetramine and Tricyanomethanide

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Triethylenetetramine (L^4) was used as a tetradentate blocking ligand that, after complexation with Ni^{II}, leaves two sites ready for ligation with tricyanomethanide. The formed binuclear complex $[L^4Ni(\mathbf{N}CC(CN)C\mathbf{N})_2NiL^4](ClO_4)_2$ exhibits a ferromagnetic coupling with $J/hc = +0.15$ cm^{-1} and $g_{Ni} = 2.126$; below 16 K, a ferromagnetic ordering is evidenced by ac magnetic susceptibility (both in-phase and out-of-phase), magnetization, field-cooled magnetization, and zero-field-cooled magnetization measurements.

The bridging ability of pseudohalide ions (both linear, CN^-, N_3^-, NCO^-, NCS^-, $NCSe^-$, CNO^-, and nonlinear, $N(CN)_2^-$, $C(CN)_3^-$, $ONC(CN)_2^-$, etc.) as well as more complex entities such as diamagnetic $[Ni(CN)_4]^{2-}$ and $[Ag(CN)_2]^-$ was utilized for a long time in designing low-dimensional materials whose magnetic properties have been extensively studied. Let us exemplify some recent investigations of magnetic properties of end-on and end-to-end azide bridged complexes,[1] complexes of $N(CN)_2^-$ (hereafter dca),[2] and complexes of $C(CN)_3^-$ (abbreviated as tcm).[3] The coordination chemistry of dca and tcm ligands has been intensively studied in a systematic way for a longer period.[4]

Oligonuclear metal complexes, in contrast to polymeric systems, can maintain the ferromagnetic interaction in orthogonal magnetic orbitals.[5] Recently, we attempted to prepare a binuclear nickel(II) complex $[L^4Ni(tcm)_2NiL^4](ClO_4)_2$, **1**, in which two pseudohalide ligands, $C(CN)_3^-$, bear the bridging functionality (L^4 = triethylenetetramine).[6] As the complex showed interesting magnetic properties, a more detailed magnetochemical investigation is promising and done in the present Communication.

The chemicals used were commercial products. $KC(CN)_3$ was prepared by literature methods.[7]

CAUTION: *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with caution.*

A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (2.5 mmol) containing triethylenetetramine (2.5 mmol) in 15 cm^3 of water was combined with $KC(CN)_3$ (2.5 mmol) in 15 cm^3 of water. Nickel hydroxide was removed by filtration, and from the filtrate, violet crystals of **1** were collected the next day. Yield: 28%. Found: C, 30.1; H, 4.99; N, 22.7; Cl, 8.9; Ni, 13.8. Calcd for $C_{20}H_{36}N_{14}Cl_2Ni_2O_8$: C, 30.5; H, 4.57; N, 24.9; Cl, 8.99 Ni, 14.9%. IR (cm^{-1}, KBr) 2243m, 2211vs, 2185vs (νCN). UV−vis (nm, MgO) 894, 554, 358.

An ac-susceptometer/magnetometer (LakeShore, model 7225) has been used in magnetization and ac-susceptibility measurements (field parameters: $f = 222$ s^{-1}, $H_{AC} = H_{DC} = 800$ A m^{-1}; correction to the underlying diamagnetism

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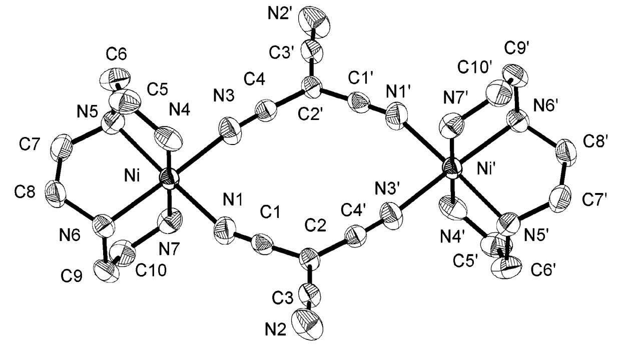

Figure 1. X-ray structure of the cationic part of **1** (hydrogen atoms omitted for clarity).

with Pascal constants). The field-cooled magnetization and zero-field-cooled magnetization measurements were done at $B = 0.01$ T. A SQUID apparatus (Quantum Design) has been used in magnetization measurements between -6 to $+6$ T.

A single crystal of **1** was mounted to a STOE-STADI-IV diffractometer (graphite monochromator, Mo Kα radiation). Corrections for Lorentz and polarization effects were applied. Direct methods and full least-squares refinement with anisotropic heavy atoms have been applied.[8] Crystal data for $C_{10}H_{18}ClN_7NiO_4$ at $T = 298$ K include the following: monoclinic, space group $P2_1/n$, $a = 7.489(1)$ Å, $b = 15.582(3)$ Å, $c = 14.643(3)$ Å, $\beta = 104.50(2)°$, $V = 1654.4(5)$ Å^3, $Z = 4$, μ(Mo Kα) = 1.364 mm^{-1}.[10] Refinement parameters follow: reflns collected/unique 5366/2814 ($R_{int} = 0.0315$); final R1/wR2 [$I > 2\sigma(I)$], 0.037/0.081; final R1/wR2 (all data), 0.058/0.093. Additional material is available from the Cambridge Crystallographic Data Centre in CIF format (CCDC number 143950).

Complex **1** possesses binuclear units and perchlorate counteranions (Figure 1). The octahedrally coordinated nickel(II) atoms are capped by the tetradentate triethylenetetramine with the terminal NH_2 groups in a *trans* position. Two remaining *cis*-positioned vertices are occupied by tcm anions that bear bridging-ligand functionality. The interatomic distances Ni−N in the chromophore $NiN_4N'_2$ are almost equal within the experimental error and amount on average to 2.099(5) Å. The bond angles N−Ni−N vary between N(6)−Ni−N(7) = 82.2(1)° and N(5)−Ni−N(7) = 98.4(1)°. The almost planar tcm utilizes two of three possible N-donors to coordinate which results in the formation of a 12-membered ring. The maximum deviation from the least-squares plane defined by all ring atoms is −0.149(3) Å for C(2).

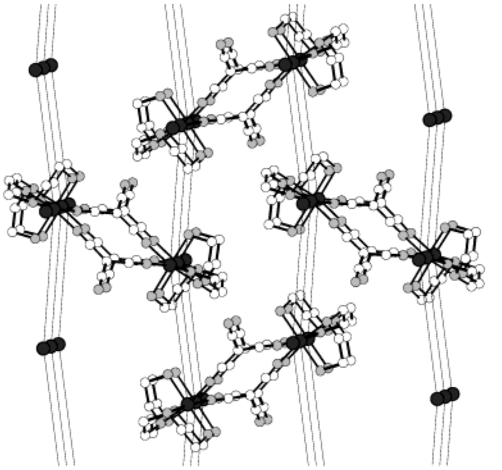

Figure 2. View to the packing of the cationic part of **1** along the *a*-axis (hydrogen atoms omitted for clarity). The solid line connects the interdimer metal centers.

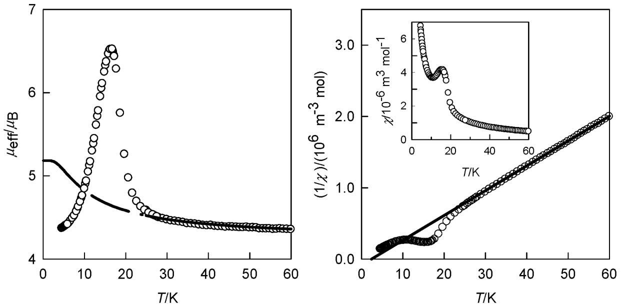

Figure 3. Temperature dependence of the magnetic functions for **1** at $B = 0.001$ T: effective magnetic moment (left, solid line shows the fitted paramagnetic response with extrapolation below 25 K); inverse susceptibility (right, regression straight line for data above 25 K); molar magnetic susceptibility (inset).

A unique feature of the crystal structure lies in the packing of the dinuclear complexes. In the *a*-direction, the complex cations form lamellar stacks in which the units $Ni(tcm)_2Ni$ are tilted with respect to the *bc*-plane: within these stacks the interdimer Ni−Ni contacts are 7.489 Å as opposed to the intradimer Ni−Ni separation of 7.265 Å. Additionally, in the *b*-direction, every Ni atom has two nearest neighbors of two different stacks with distances of 7.859 Å (Figure 2).

Only weak intermolecular hydrogen bonds of the types N−H···O (perchlorate) and N−H···N (uncoordinated CN group of tcm) with NH and NH_2 groups [N(4), N(5), N(6), N(7)] of the amine but with distances between proton donor and acceptor longer than 3 Å hold the structure together.

The magnetic properties closely resemble the structural motif of the complex. The effective magnetic moment for **1** is slightly increasing on cooling from the value of $\mu_{eff} = 4.34\ \mu_B$ at $T = 80$ K to the value of $\mu_{eff} = 4.59\ \mu_B$ at $T = 25$ K (Figure 3). On further cooling, however, a substantial increase of the effective magnetic moment occurs: $\mu_{eff} = 6.53\ \mu_B$ at $T = 16.2$ K. Evidently, a ferromagnetic ordering occurs probably due to rather short interdimer contacts (7.5 Å) within the planes. However, below 16.5 K a decrease of the effective magnetic moment occurs indicating a kind of an antiferromagnetic ordering among lamellar blocks. Analogous behavior, for instance, has been reported for a two-

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dimensional honeycomb network based on $[Fe(CN)_6]^{3-}$ and $[NiL^4]^{2+}$ building blocks, and a polymeric sheetlike structure of $[NiL^2{}_2]_2[Fe(CN)_6]X$.[9]

The higher-temperature data set (25−85 K) corresponding to a paramagnetic behavior can be successfully fitted using an isotropic exchange Hamiltonian.[10]

$$\hat{H} = -J\hbar^{-2}(\hat{S}_A \cdot \hat{S}_B) + \mu_B \hbar^{-1} B g_{Ni}(\hat{S}_{A,z} + \hat{S}_{B,z}) - (zJ')\hbar^{-1}\langle S_z\rangle \hat{S}_z$$

A fitting procedure gave the magnetic parameters $J/hc = +3.75$ cm^{-1} and $g_{Ni} = 2.119$ ($R = 0.0088$). The fit can be improved by adding the molecular field correction: $J/hc = +0.15$ cm^{-1}, $g_{Ni} = 2.126$, and $zJ'/hc = +0.071$ cm^{-1} ($R = 0.0067$).

Slight ferromagnetic nature of the exchange coupling constant results from a partial cancellation of the ferromagnetic and antiferromagnetic contributions. In the present case of an odd number of spacers (atoms) separating the metal centers, the ferromagnetic portion becomes substantial, and the spin-polarization mechanism applies.[11] The counterpart antiferromagnetic portion, on the contrary, could be suppressed owing to large intradimer Ni−Ni separation. While the intradimer coupling constant refers to a through-orbital interaction, the molecular-field exchange parameter accounts to weak through-space (dipole−dipole) interactions among dinuclear units; there are six neighboring dimers within the planes so that the number of neighbors is $z = 6 + 2$ and then J(intradimer) $\ll J'$(molecular-field).

A reliable determination of the single-ion anisotropy (the axial zero-field splitting) parameter D_{Ni} is not possible in the present case as the low-temperature paramagnetic signal is overlapped by a much stronger response from the long-range ordering below 25 K.

The magnetization measurements until $B = 5.5$ T bring evidence for a saturation at low temperature. The limiting value of magnetization per particle, $M_{mol}/N_A = 4.0\ \mu_B$, matches the $S = 2$ ground state of the complex (Figure 4). In this sense, the behavior of **1** is analogous to the dinuclear complex $[Cu(C(CN)_3)_2(Hpz)_3]_2$ presented elsewhere.[3d] The hysteresis loop is seen already at $T = 12$ K, and this becomes more pronounced with temperature lowering. However, the coercivity is quite small.

The field-cooled magnetization data are presented in Figure 5 along with the zero-field-cooled magnetization data. The intercept of the curves is an indicator of the ordering temperature ($T_c = 16$ K) and the long-range ordering itself. The ac-susceptibility measurements in the dual mode show that the imaginary (out-of-phase) susceptibility passes through a maximum at the ordering temperature. As the maximum of the out-of-phase susceptibility is frequency-independent, no feature of a single molecule magnet was found.

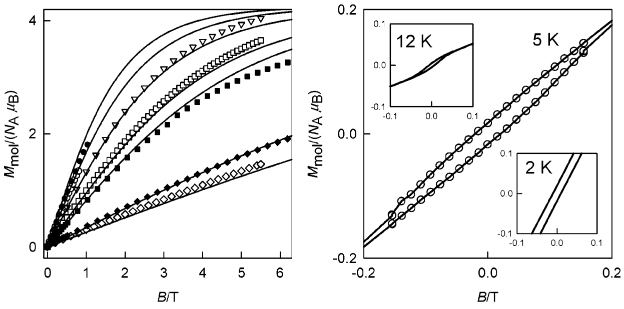

Figure 4. Left: field dependence of the magnetization for **1** at various temperatures, 2.0, 2.4, 3.1, 4.3, 5.0, 12.0, and 15.8 K. Solid lines show theoretical magnetization based upon the partition function with $g = 2.126$ and $J/hc = 0.15$ cm^{-1}. Right: the hysteresis loop at different temperatures, $T = 5.0$ K (center), 12.0 K (top inset), 2.0 K (bottom inset).

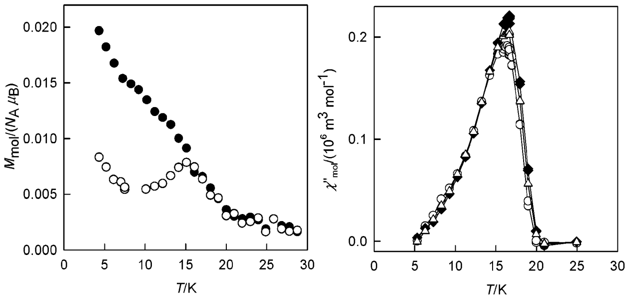

Figure 5. Left: temperature variation of the field-cooled magnetization (●) and zero-field-cooled magnetization (○) for **1** at $B = 0.01$ T. Right: the imaginary (out-of phase) ac susceptibility of **1** at different frequencies, $f = 16$ (○), 222 (gray △), and 1000 (◆) s^{-1}.

In conclusion, the prepared binuclear Ni(II) complex belongs to the class of ferromagnetically coupled dimers with a rather small coupling constant. A ferromagnetic ordering applies below 16 K as evidenced from the out-of-phase ac susceptibility, field-cooled magnetization, and zero-field-cooled magnetization, as well as by the hysteresis effect seen already at $T = 12$ K and below.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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