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A novel chloro-bridged tetranuclear cadmium(II) cluster with pyridyl-substituted nitronyl nitroxide: structure and magnetic properties

Chin-Jhan Lee [a], Ho-Hsiang Wei [b,*], Gene-Hsiang Lee [c], Yu Wang [c]

[a] Deh-Yu College of Nursing and Management, Keelung, Taiwan, ROC
[b] Department of Chemistry, Tamkang University, Tamsui, Taiwan, ROC
[c] Instrumental Center, College of Science, National Taiwan University, Taipei, Taiwan, ROC

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Abstract

A tetranuclear cadmium(II) complex of 2(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1 H-imidazol-1-oxy 3-N-oxide (NIToPy) with $CdCl_2$, $[Cd_4Cl_8(NIToPy)_4]$, has been structurally and magnetically characterized. The structure is based on a novel chloro-bridged tetranuclear cadmium quasi-cubane cluster, in which each cadmium atom is chelated by one NIToPy radical, and coordinated with four bridging chlorine atoms. The temperature dependence of the magnetic susceptibility measurements shows a weak ferromagnetic coupling between the radicals. An excellent simulation of the experimental data with the prism type four spins Hamiltonian $H = -2J_1(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4) - 2J_2S_2S_4$ obtained the parameters: $J_1 = 1.12$ cm^{-1}, $J_2 = -0.20$ cm^{-1}, and $g = 2.04$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Cadmium compound; Nitronyl nitroxide; Crystal structure; Magnetic properties

When the electron spins of two unpaired electrons are placed in proximity and allowed to interact as in organic radicals, the Columbic repulsion between the two electron spins lifts the zeroth-order degeneracy and gives rise to singlet and triplet states of different total energy for these radical compounds. It has been established that an inter- and/or intra-molecular exchange coupling among the spins and their higher dimensional arrangement in space are required to order them at finite temperature [1]. On the basis of this consideration, the radical centers should have to be placed in proximity in order to have strongly magnetic ordering. Many efforts have been, therefore, devoted to synthesize di-, oligo-, and polyradicals having macroscopic spin alignment with the aids of connecting through the π-conjugated moieties [2], or complexation with metal ions [2,3].

Diamagnetic metal ions are believed not to mediate magnetic interactions. Several diamagnetic metal complexes with organic radical ligands however, have shown that antiferro- or ferromagnetic interactions were operative through the diamagnetic metal ions; such as alkali metals [4,5], Ga(III) [6], Ti(IV) [7], Cu(I) [8], and Hg(II) [9]. The strength of inter-radical magnetic exchange interactions depends on metal ions and coordination geometries. $[M^{III}(3,6\text{-dbsq})_3]$ [6] (M = Al, and Ga; 3,6-dbsq = 3,6-di-tert-butylsemiquinone) and $[Ga^{III}(3,5\text{-dtbsq})_3]$ [6] (3,5-dtbsq = 3,5-di-tert-butyl-1,2-benzosemiquinone) showed weak ferromagnetic interactions, while $[M^{IV}(\text{Cat–N–SQ})_2]$ (M = Ti, Ge, and Sn) [7] showed strong ferromagnetic interactions between radical ligands. It is also showed that a copper(I) ion in $[Cu(\mu\text{-}X)(\text{iminonitroxide})]_2$ (X = Br or I) mediates intermolecular ferromagnetic and antiferromagnetic interactions [8b].

Accordingly, if organic radicals are introduced into the bridged cadmium(II) cluster or network, interesting magnetic behaviors might be obtained. Complexes of the type CdX_2 (X = Cl or Br) with organic bases (e.g., pyridine) typically form one- or three-dimensional halogen-bridged chain or cluster compounds with six-coordination cadmium(II) [10]. Pyridyl-substituted nitronyl nitroxide, 2(2-pyridyl)4,4,5,5-tetramethyl-4,5-dihydro-1 H-imidazol-1-oxy-3-N-oxide (NIToPy), is a paramagnetic chelate ligand which can mediate a magnetic exchange interaction when bound to paramagnetic transition-metal halides such as $NiCl_2$(NIToPy) and

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[*] Corresponding author. Fax: +886-2-262-09-924.
E-mail address: tkwei@mail.tku.edu.tw (H.-H. Wei).

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$MnCl_2$(NIToPy) [11]. Nevertheless, the use of diamagnetic metal ions has not been widespread.

Recently, we have reported that a one-dimensional cadmium(II) complex $[(CdCl_2)_3(NIToPy)_2(C_2H_5OH)_2]$ revealed a weak antiferromagnetic interaction between two nitroxide radicals [12]. In exploring the cadmium chemistry of organic radicals, we have made the unusual observation that the first example of a novel chloro-bridged quasi-cubane cadmium cluster with NIToPy radicals and shows a weak ferromagnetic coupling in the temperature dependence of magnetic susceptibility. The complex **1** $[Cd_4Cl_8(NIToPy)_4]$ was obtained by dissolving of $CdCl_2$ in methanol and followed by addition of NIToPy [13] in dichloromethane. Dark-blue crystals were formed from the deep blue solution. [1]

The X-ray crystal structure at 298 and 90 K (Fig. 1) of the complex **1** [2] revealed that the molecule possesses centrosymmetric tetranuclear cluster structure with $Cd_4(Cl)_2(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)_2$ core and comprises four NIToPy free radicals. Four cadmium atoms arrange as a prism form in space and there are two different coordination enviroments for the four Cd atoms, one is formed by the atoms of O and N from NIToPy ligand, two μ_3-Cl atoms atoms and two μ-Cl atoms such as for Cd(1), whereas the other one is formed by a chelating NIToPy ligand, one terminal Cl, one μ_3-Cl atom and two μ-Cl atoms such as for Cd(2). Here, the bond distances and angles of the complex determinated at 90 K are discussed. The terminal Cd(2)–Cl(4) bond distance [2.488(2) Å] is shorter than the mean Cd–Cl(μ) bond distance [2.592(2) Å] and the mean Cd–Cl(μ_3) bond distance [2.741(2) Å]. The shortest intra-molecular Cd(1)···Cd(1A) separation is 3.800 Å. The mean Cd–N and Cd–O bond distances are 2.416(6) and 2.327(4) Å, respectively. The O(1)–N(2)–C(6)–N(3)–O(2) and the O(4)–N(6)–C(18)–N(5)–O(3) planes of the nitronyl nitroxide group make dihedral angles of 37.1(2)° and 31.4(2)°, respectively, with the corresponding pyridine rings. Thus the NO radical groups of NIToPy in the coordination sphere are not in same plane and not in same direction to each other. [3] The inter-molecular closest contact between O···O of NO groups is 4.344(2) Å.

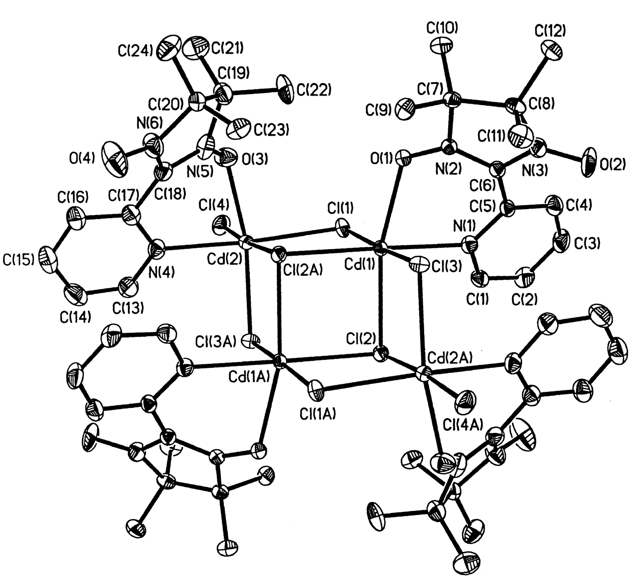

Fig. 1. ORTEP drawing (thermal ellipsoids drawn at the 50% probability level) of $[Cd_4Cl_8(NIToPy)_4]$ **1**. Selected bond distances (Å): Cd(1)–O(1) 2.326(4), Cd(1)–N(1) 2.389(14), Cd(1)–Cl(1) 2.586(2), Cd(1)–Cl(2) 2.669(2), Cd(1)–Cl(3) 2.592(2), Cd(2)–O(3) 2.327(3), Cd(2)–N(4) 2.444(6), Cd(2)–Cl(4) 2.488(2), Cd(2)–Cl(2A) 2.900(2), N(2)–O(1) 1.303(6), N(5)–O(3) 1.279(7). Selected bond angles (°): O(1)–Cd(1)–Cl(2) 166.08(11), N(1)–Cd(1)–Cl(2A) 177.45(13), Cl(3)–Cd(1)–Cl(1) 175.49(5), O(3)–Cd(2)–Cl(3A) 161.24(13), Cl(4)–Cd(2)–Cl(2A) 174.92(4), N(4)–Cd(2)–Cl(1) 162.53(14), Cd(1)–Cl(1)–Cd(2) 101.78(5), Cd(1)–Cl(2)–Cd(2) 90.51(14), Cl(1)–Cd(2)–Cl(2A) 79.89 (4), O(1)–Cd(1)–N(1) 76.8(2), O(3)–Cd(2)–N(4) 76.7(2).

The X-band EPR spectrum (9.78 GHz) of powder sample at 290 K exhibits a narrow and shape single signal with $g = 2.04$. The temperature dependence of both the product $\chi_m T$ and the molar magnetic susceptibility χ_m of **1** are represented in Fig. 2. [4] The $\chi_m T$ value was 1.43 cm^3 K mol^{-1} at 300 K($\mu_{eff} = 3.38\mu_B$); on lowering the temperature, the $\chi_m T$ increased, reaching a maximum value of 1.63 cm^3 K mol^{-1}($\mu_{eff} = 3.61\mu_B$) at 15 K, and then decreased. The maximum $\chi_m T$ value of 1.63 cm^3 K mol^{-1}($\mu_{eff} = 3.61\mu_B$) that was observed is larger than the non-coupled four $S = 1/2$ systems (1.5 cm^3 K mol^{-1}). The structure of **1** consists of four Cd atoms and four boned-nitroxide oxygens to take a centrosymmetrical prism type arrangement by X-ray analysis. Therefore two ways of theoretical calculations are adopted. We first considered the exchange interaction as the leading term with the corresponding two spins $S_1 = S_2 = 1/2$ of a Hamiltonian $H = -2JS_1S_2$ [14]. A poor fit with $J = 0.21$ cm^{-1}, and an inter-cluster

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[1] Anal. found: C 34.36; H 3.86; N 9.92%. Calcd. for $C_{48}H_{64}Cd_4C_{18}N_{12}O_8$: C 34.48; H 3.83; N 10.06%.

[2] Crystal data determinated at 90 K for 1: $[Cd_4Cl_8(NIToPy)_4]$: $C_{48}H_{64}Cd_4Cl_8N_{12}O_8$, $M = 1670.31$, monoclinic, space group $P2_1/n$, $a = 14.4568(1)$ Å, $b = 10.1616(1)$ Å, $c = 21.8609(3)$ Å, $\beta = 107.322(1)^\circ$, $V = 3065.81(1)$ Å^3, $Z = 2$, and $D_c = 1.809$ g cm^{-3}; crystal dimensions 0.32 × 0.20 × 0.18 mm. λ (MoKα) = 0.71073 Å. The structure was solved by direct methods and Fourier techniques, and refined by full-matrix least-squares on F^2 using SHELXL-93 (G.M. Sheldrick, University of Göhingen 1993). All non-hydrogen atoms were readily located and refined with anisotropic thermal parameters. The refinement of 362 parameters covered to $R(F) = 0.054$ and $R_w(F^2) = 0.121$ with $I > 2\sigma(I)$.

[3] The torsion angles for N(2)–O(1) vs. N(2A)–O(1A) and N(5)–O(3) vs. N(5A)–O(3A) are 180°, whereas N(2)–O(1) vs. N(5A)–O(3A) and N(2A)–O(1A) vs. N(5)–O(3) are −103.5° and 103.5°, respectively.

[4] The magnetic susceptibilities of powdered sample of **1** were recorded on a Quantum Design model MPMS computer-controlled SQUID magnetometer in the temperature range 4–300 K at a field of 1 T.

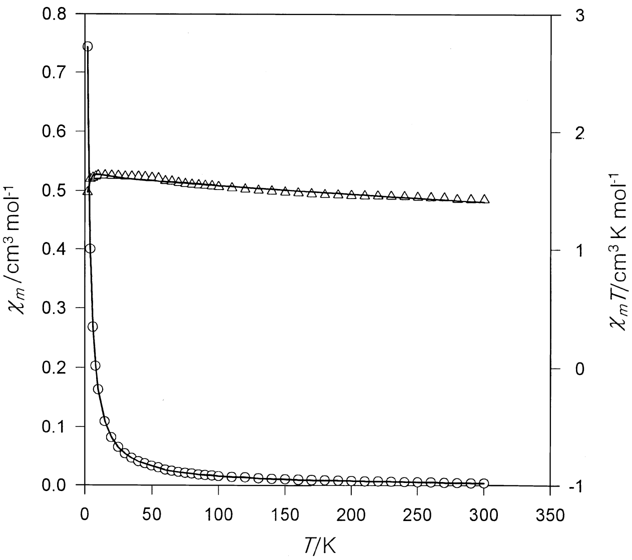

Fig. 2. Plots of χ_{m} (○) and $\chi_{\mathrm{m}}T(\Delta)$ vs T for crystalline sample of **1**.

interaction term of $\theta = 0$ are obtained. Finally we use a four spins arranged prism model as in the cluster. The spin Hamiltonian $H = -2J_1(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4) -2J_2S_2S_4$ is adopted [15], where J_1 and J_2 are the spin coupling constants between N(5)–O(3)$\cdots$O(1)–N(2) and N(2)–O(1)$\cdots$O(1A)–N(2A), respectively. An excellent simulation of the experimental magnetic data is obtained with $J_1 = 1.12$ cm^{-1}, $J_2 = -0.20$ cm^{-1}, and $g = 2.04$ (from EPR).

The structural analysis of **1** at room temperature and at 90 K shows that the NO radicals of NIToPy ligands are aggregated in the cadmium cluster, and the directions of NO groups of intra-cluster are not same directions to each other. Therefore, the preliminary mechanistic magnetic interactions in **1** can be interpreted to be: (i) the long-range spin polarization effect [16] through the NO–Cd–Cl–Cd–ON framework and spin-polarization through the closest contact between uncoordinated N–O groups and hydrogen atoms of the neighbor NIToPy moiety or; (ii) the dipole–dipole interactions between intra- and inter-cluster nitroxide radicals. The decisive mechanism will be discussed elsewhere. The present finding of temperature-dependent magnetic susceptibility revealed that the introduction of diamagnetic metal ion into organic radicals has potentiality for constructing a magnetically ordered molecular system.

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