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Magnetic Study on a Two-Dimensional Coordination Polymer with Mixed Bridging Ligands

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A two-dimensional coordination polymer, $[Co(\mu_{1,3}\text{-SCN})_2(\mu_{1,6}\text{-dmpzdo})]_n$ (where dmpzdo = 2,5-dimethylpyrazine-1,4-dioxide), has been synthesized and its crystal structure determined by X-ray crystallography. In the complex, the adjacent Co(II) ions are coordinated by $\mu_{1,3}$-SCN$^-$ bridging ligands which forms a one-dimensional chain along the *a* axis; the one-dimensional chains are further connected by $\mu_{1,6}$-dmpzdo bridging ligands which leads to the formation of a two-dimensional layer on the *ac* plane. The theoretical calculations reveal that a ferromagnetic coupling exists between the $\mu_{1,3}$-SCN$^-$ bridging Co(II) ions and an anti-ferromagnetic interaction between the $\mu_{1,6}$-dmpzdo bridging Co(II) ions, and the anti-ferromagnetic interaction is stronger than the ferromagnetic interaction. The fitting of the variable-temperature (34−300 K) magnetic susceptibilities reveals that there is an anti-ferromagnetic coupling between the bridging Co(II) ions with the magnetic coupling constant $J = -3.52$ cm^{-1}.

Introduction

For a long time, the field of molecular magnetism has attracted considerable attention, and major advances have been made in both their theoretical description and their application as new molecular-based materials.[1−3] To evaluate the magnetic coupling properties of bridging metal ions, the fitting of experimental susceptibility data is necessary, and in this area, many fitting models or fitting formulas have been derived and used. However, for the complexes with a two-dimensional bridging structure or a three-dimensional bridging structure, no fitting formula is available and it still is hard to crack the data. Recently, to handle this difficult problem, we have tried to simplify the complicated magnetic interactions into binuclear units and then compare the magnetic coupling intensities between different binuclear units by using theoretical calculations. After that, a proper fitting formula is selected and is used to fit the experimental values. This approximate manner sometimes can give the satisfied results and especially for the complex with mixed bridging ligands.[4]

Interest in the magnetostructure studies of the complexes with two-dimensional bridging structures resulted in our designing, synthesizing, and studying the title two-dimensional structural complex with the mixed bridging ligands. In the magnetostructure studies area, it is a completely new way to handle the magnetic couplings of two-dimensional bridge structural complexes by using the structure simplification, theoretical calculations, and experimental fitting as mentioned above. This paper deals with the magnetostructure study of binuclear Co(II) complexes with $\mu_{1,3}$-SCN$^-$ and 2,5-dimethylpyrazine-1,4-dioxide as bridging ligands, respectively, by using theoretical calculations, and in this area, this is the first time one has dealt with the complexes of pyrazine-1,4-dioxide and its derivatives as bridging ligands, although much work has been done with binuclear complexes with μ-azido,[5] μ-hydroxyl,[6] μ-halide,[7,8] $\mu_{1,3}$-NCS$^-$, and so on, as bridged ligands. Here, we report the synthesis, the structure, the theoretical calculations, and the experimental fitting of the title two-dimensional bridging structural Co(II) complex.

Experimental Section

Materials. 2,5-Dimethylpyrazine-1,4-dioxide was synthesized according to the literal method,[9] and all other chemicals are analytical grade and used without further purification.

Preparation of $[Co(\mu_{1,6}\text{-dmpzdo})(\mu_{1,3}\text{-SCN})_2]_n$. $Co(ClO_4)_2 \cdot 6H_2O$ (0.3848 g, 1.05×10^{-3} mol), NaSCN (0.1705 g, 2.10×10^{-3} mol), and 2,5-dimethylpyrazine-1,4-dioxide (0.1474 g, 1.05×10^{-3} mol) were each dissolved in 8 mL of H_2O, and then, the three kinds of solutions were mixed together. The brown single crystals were obtained after the mixed solution was allowed to stand slow evaporation for about 1 month at room temperature. Yield: 53%. Anal. Calcd (found) for $C_8H_8CoN_4O_2S_2$ (fw 315.235): C, 30.48 (29.85); H, 2.56 (2.28); N, 17.77 (17.31); Co, 18.70 (18.98). IR (cm^{-1}): 2115 s, 1627 m, 1515 m, 1401 m, 1176 s, 879 m, 710 m.

Physical Measurements. Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the 4000−500 cm^{-1} region using KBr disks. C, H, and N elemental analyses were carried out on a Perkin-Elmer 240 instrument. Variable-temperature magnetic susceptibilities of microcrystalline powder samples were measured in a magnetic field of 3 KOe in the temperature range 4−300 K on a SQUID magnetometer. The data were corrected for magnetizaction of the sample holder and for diamagnetic contributions which were estimated from Pascal's constants.

Density Function Calculation. Two separate calculation methods were carried out by means of density functional theory:[10] one is the hybrid B3LYP method,[11] as implemented in

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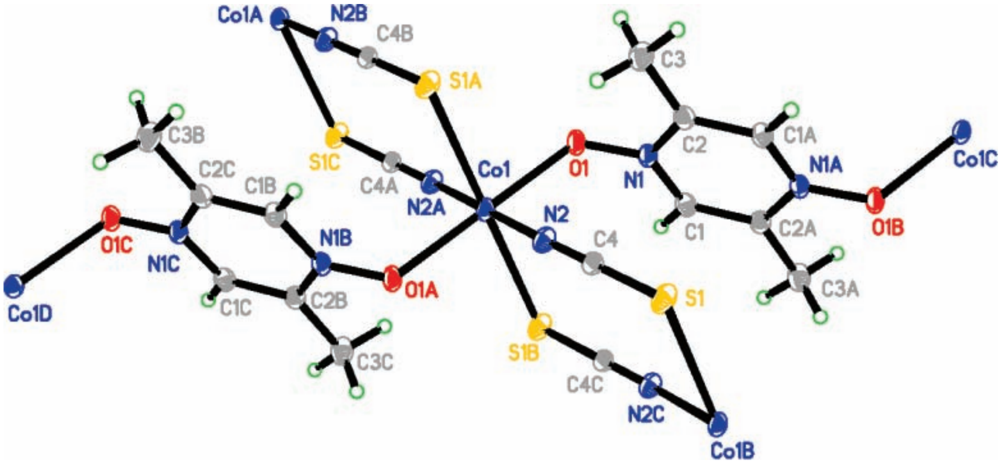

Figure 1. Coordination diagram of the complex with the atom numbering scheme.

Gaussian 98,[12] mixing the exact Hartree−Fock exchange[13] with Becke's expression for the exchange and with the Lee−Yang−Parr correlation functional.[14] Double-ζ quality and triple-ζ quality basis sets proposed by Ahlrichs[15] have been employed for nonmetallic and metallic atoms, respectively. Another is Vosko, Wilk, and Nusair's (VWN) function which was used for local spin density approximation (LSDA)[16] with the Amsterdam density functional (ADF) package (version 2.0.1). Generalized gradient correlations have been introduced by using the Becke exchange function[13] and the Perdew correlation function.[17] IV basis sets in ADF containing triple-ζ basis sets and a polarization function from H to Ar were used for all atoms in the systems. The frozen core (FC) approximation for the inner core electrons was employed. The orbitals up to 2p for S and Co atoms and 1s for C, N, and O atoms were kept frozen. The numerical integration procedure applied for the calculation is the polyhedron method developed by Velde and co-workers.[18,19] All of the calculations were done on an SGI O2100 server.

X-ray Crystallographic Analysis of the Complex. A single crystal of dimensions 0.18 mm × 0.11 mm × 0.09 mm was selected and subsequently glued to the tip of a glass fiber. The determination of the crystal structure at 25 °C was carried out with an X-ray diffractometer, model Bruker Smart-1000 CCD, using graphite-monochromatic Mo Kα radiation ($\lambda = 0.710\ 73$ Å). Corrections for *Lp* factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and included in the final cycles of refinement using a riding model. The programs for structure solution and refinement were SHELXTL (Bruker, 2001). The crystal belongs to monoclinic space group $P2_1/c$, with $a = 5.7128(14)$ Å, $b = 14.346(4)$ Å, $c = 6.9722(17)$ Å, $\beta = 97.468(3)°$, $V = 566.6(2)$ Å^3, empirical formula $C_8H_8CoN_4O_2S_2$, molecular weight 315.235, $D_c = 1.848$ g/cm^3, $F(000) = 318$, θ range 2.84−25.50°, index ranges $-6 \le h \le 4$, $-17 \le k \le 17$, $-8 \le l \le 8$. A total of 2988 reflections were collected, and 1054 were independent ($R_{int} = 0.0219$), of which 941 observed reflections with $I > 2\sigma(I)$ were used in the succeeding refinement. The final refinement including hydrogen atoms converged to $R = 0.0317$, $wR = 0.0771$, $(\Delta\rho)_{max} = 0.308$ e/Å^3, and $(\Delta\rho)_{min} = -0.274$ e/Å^3. The deposition number of the crystal at the CCDC is 249998.

Results and Discussion

Crystal Structure. Figure 1 shows the coordination diagram with the atom numbering scheme. It displays that the Co1 atom is coordinated by the O1, O1A, N2, N2A, S1A, and S1B atoms, in which the O1 and O1A atoms are from the two $\mu_{1,6}$-dmpzdo bridging ligands and the other four atoms come from the four $\mu_{1,3}$-SCN$^-$ bridging ligands, respectively. The data in Table 1 indicate that the coordination environment of the Co1 atom is a distorted octahedron geometry. Figure 1 also reveals that in this crystal two kinds of bridging ligands exist, namely, $\mu_{1,3}$-SCN$^-$ bridging ligand and $\mu_{1,6}$-dmpzdo bridging ligand, and two adjacent Co(II) ions with a Co···Co separation of 5.713 Å are bridged by two $\mu_{1,3}$-SCN$^-$ bridging ligands which forms a binuclear unit. The binuclear units connect each other into a one-dimensional chain along the *a* axis, and all of the atoms from the one-dimensional chain define a plane within ±0.0644 Å with a maximum deviation of −0.0959 Å for the N2 atom and the plane is located on the *ab* plane. The one-dimensional chains are further connected by the coordination of $\mu_{1,6}$-dmpzdo bridging ligands with Co(II) ions, and that leads to the formation of a two-dimensional sheet on the *ac* plane. The distance between the $\mu_{1,6}$-dmpzdo bridging Co(II) ions is 6.9722(17) Å. All of the non-hydrogen atoms from the $\mu_{1,6}$-dmpzdo bridging ligand lie on a plane, and the dihedral angle between the plane of the $\mu_{1,6}$-dmpzdo bridging ligand and the plane of the one-dimensional chain is 29.2°. Figure 2 shows that a 22-membered ring is fabricated by two $\mu_{1,3}$-SCN$^-$ bridging ligands, two $\mu_{1,6}$-dmpzdo bridging ligands, and four Co(II) ions, and in the ring, the maximum distance between the Co(II) ions is about 12.588 Å, and the rings as subunits are further assembled into a 2D sheet.

TABLE 1: Selected Bond Lengths (Å) and Angles (deg) for the Complex[a]

Co1−N2	2.033(2)	Co1−O1	2.0900(19)	Co1−S1A	2.6446(9)
N2−Co1−O1A	89.67(8)	N2−Co1−O1	90.33(8)		
N2−Co1−S1B	90.84(6)	N2−Co1−S1A	89.16(6)		
O1−Co1−S1A	87.90(5)	O1−Co1−S1B	92.10(5)		

[a] Symmetry code. N2A and O1A: $-x, -y + 2, -z$. S1A: $x - 1, y, z$. S1B: $-x + 1, -y + 2, -z$.

Theoretical Study on Magnetic Interaction. In this complex, two pathways that may lead to the magnetic interactions between the bridged Co(II) ions exist, namely, the magnetic coupling can be mediated by $\mu_{1,6}$-dmpzdo bridging ligands or by $\mu_{1,3}$-SCN$^-$ bridging ligands. To understand which pathway is more effective, the density function calculations were performed on the binuclear model complexes [Co$_2$($\mu_{1,6}$-dmpzdo)(dmpzdo)$_2$(SCN)$_4$(NH$_3$)$_4$] and [Co$_2$($\mu_{1,3}$-SCN)$_2$(dmpzdo)$_4$(SCN)$_2$(NH$_3$)$_2$], as shown in Figures 3 and 4, respectively, and the calculation was constrained by the data of the bond lengths and the angles which are from the X-ray structures of the present complex. The calculations are based on Noodelmann's sugges-

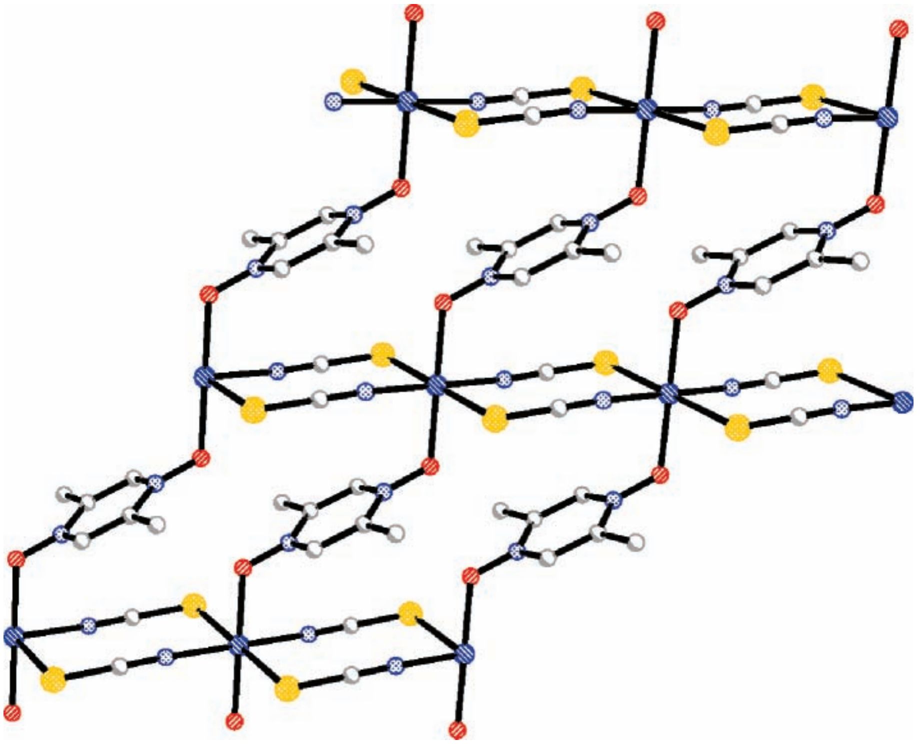

Figure 2. 22-Membered ring and the two-dimensional sheet.

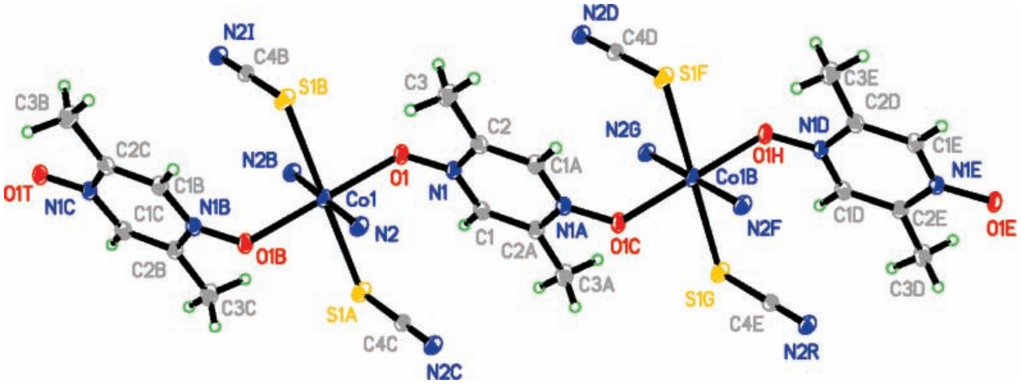

Figure 3. The binuclear model complex $[Co_2(\mu_{1,6}\text{-dmpzdo})(\text{dmpzdo})_2(SCN)_4(NH_3)_4]$ (the N2, N2B, N2G, and N2F atoms stand for the NH_3 molecule, respectively).

tions[20,21] and the model of binuclear Co(II) Hamiltonians, namely, $H = -2JS_1S_2$, in which S_1 and S_2 stand for the spin operators of the Co(II) ion and $S_1 = S_2 = {}^3/_2$. It means that the magnetic coupling constants for the binuclear Co(II) system can be obtained using the expression $E(\text{HS}) - E(\text{BS}) = -9J$, where $E(\text{HS})$ and $E(\text{BS})$ represent the energies of the quintet and broken-symmetry states, respectively. The calculations gave the coupling constants $J = -88.84\ \text{cm}^{-1}$ for the model complex $[Co_2(\mu_{1,6}\text{-dmpzdo})(\text{dmpzdo})_2(SCN)_4(NH_3)_4]$ and $J = 6.54\ \text{cm}^{-1}$ for the model complex $[Co_2(\mu_{1,3}\text{-SCN})_2(\text{dmpzdo})_4(SCN)_2(NH_3)_2]$.

For a binuclear transition metal complex, the following equation has also been advocated by Ruiz et al.[22]

$$J = \frac{2(E_{\text{BS}} - E_{\text{HS}})}{S_{\text{HS}}(S_{\text{HS}} + 1)}$$

Using the combination of a hybrid B3LYP function with double-ζ quality and triple-ζ quality basis sets for nonmetallic and metallic atoms, respectively, as implemented in the Gaussian 98 program, the calculations reveal that the magnetic coupling constants for the model complexes $[Co_2(\mu_{1,3}\text{-SCN})_2(\text{dmpzdo})_4(SCN)_2(NH_3)_2]$ and $[Co_2(\mu_{1,6}\text{-dmpzdo})(\text{dmpzdo})_2(SCN)_4(NH_3)_4]$ are $J = 463.40\ \text{cm}^{-1}$ and $J = -503.94\ \text{cm}^{-1}$, respectively.

The calculations above clearly indicate that an anti-ferromagnetic interaction exists between $\mu_{1,6}$-dmpzdo bridging Co(II) ions, whereas the $\mu_{1,3}$-SCN^- bridging ligand led to the ferromagnetic coupling. The calculations also indicate that the anti-ferromagnetic coupling is stronger than the ferromagnetic interaction, and it is reasonable that the complex should display an anti-ferromagnetic interaction.

Tables 2 and 3 show the spin density corresponding to the ground states for two models, respectively, which is from the calculation of the ADF program. Comparing the spin density values in Tables 2 and 3, it can be known that the spin density on the Co(II) atoms from Table 3 is larger than that from Table 2. The smaller spin density means larger electron delocalization, and the larger delocalization implies stronger magnetic coupling; namely, the magnetic interaction from $\mu_{1,6}$-dmpzdo-bridged Co(II) ions is stronger than that from the $\mu_{1,3}$-SCN^--bridged Co(II) ions, which is consistent with the calculated J values mentioned above.

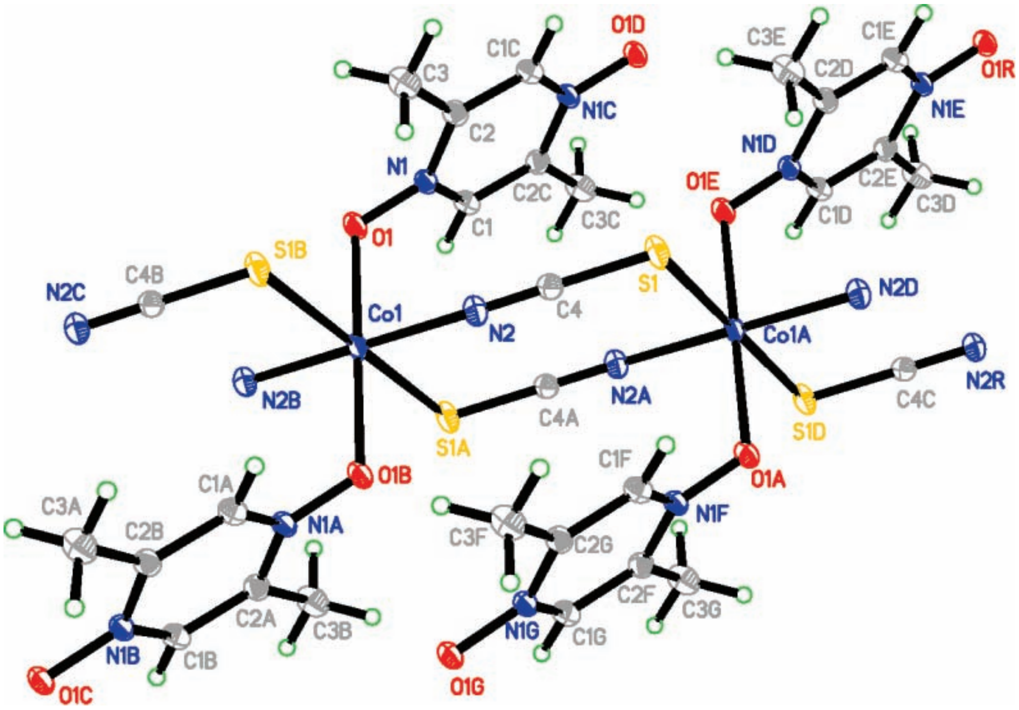

Figure 4. The binuclear model complex [$Co_2(\mu_{1,3}\text{-SCN})_2(\text{dmpzdo})_4(\text{SCN})_2(\text{NH}_3)_2$] (the N2B and N2D atoms stand for the NH_3 molecule, respectively).

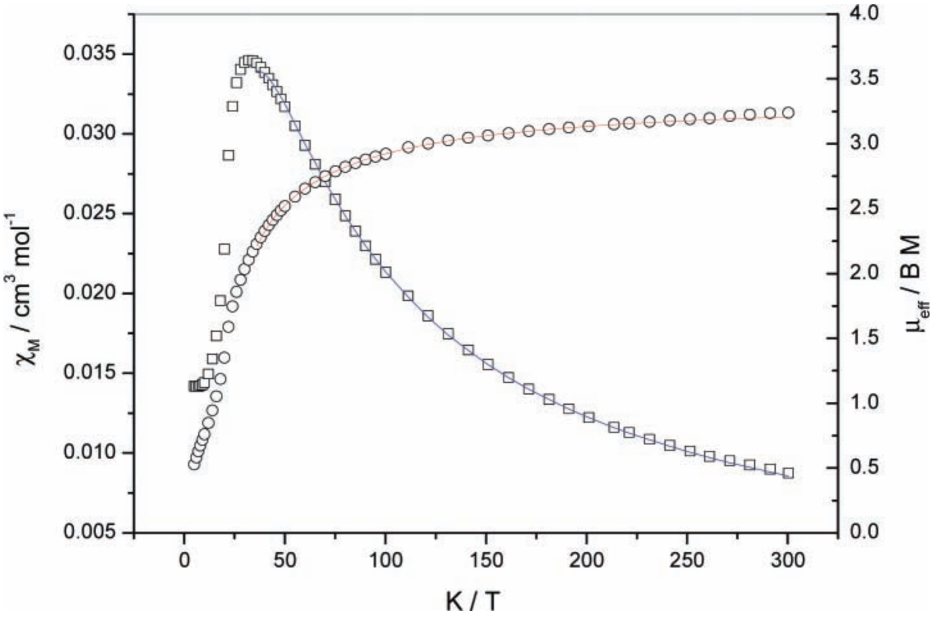

Figure 5. Plots of χ_M (open squares for experimental data, blue line for theoretical value) and μ_{eff} (open circles for experimental data, red line for theoretical value) versus T for the complex.

TABLE 2: Calculated Atom Spin Population for the Binuclear Model Complex [$Co_2(\mu_{1,6}\text{-dmpzdo})(\text{dmpzdo})_2(\text{SCN})_4(\text{NH}_3)_4$]

atom	spin density	atom	spin density	atom	spin density
Co1	−2.2018	O1	−0.0414	O1B	-0.0106
N1	−0.0283	N2	−0.0339	N2B	-0.0340
S1A	−0.0857	S1B	−0.0973		
Co1B	2.1968	O1C	0.0146	O1H	0.0086
N1A	0.0325	N2F	0.0244	N2G	0.0315
S1F	0.0913	S1G	0.0968		

TABLE 3: Calculated Atom Spin Population for the Binuclear Model Complex [$Co_2(\mu_{1,3}\text{-SCN})_2(\text{dmpzdo})_4(\text{SCN})_2(\text{NH}_3)_2$]

atom	spin density	atom	spin density	atom	spin density
Co1	2.4896	O1	0.0808	O1B	0.0893
N2	0.0592	N2B	0.0875	S1A	0.0648
S1B	0.0748				
Co1A	2.4896	O1A	0.0808	O1E	0.1008
N2A	0.0592	N2D	0.0425	S1	0.0648
S1D	0.1171				

Experimental Data Fitting Results. The variable-temperature (4−300 K) magnetic measurements were made, and the experimental results are shown in Figure 5, where χ_M is the molar magnetic susceptibility per Co(II) unit, μ_{eff} is the magnetic moment per Co(II) ion, and the data have been corrected for diamagnetism. Figure 5 displays that the χ_M value increases with decreasing temperature, reaches a maximum at $T_N = 32$ K, and then follows a sharp decrease. The μ_{eff} value at 300 K is 4.58 μ_B, which is larger than the expected value for an isolated mononuclear Co(II) ion (3.87 μ_B for $g_{av} = 2$) at room temperature, and the μ_{eff} value decreases with temperature drop and reaches a minimum of 0.75 μ_{B} at 4.93 K, which implies an anti-ferromagnetic exchange between the bridged Co(II) ions. Because no fitting formula is available for the two-dimensional complex to date and according to the information of the calculations above, it is known that the magnetic coupling from the $\mu_{1,6}$-dmpzdo bridging ligand is more effective, and therefore, we have tried to fit the experimental susceptibility data using the uniform one-dimensional chain equation (eq 2),[23] which derived from the classic spin Heisenberg Hamiltonian (eq 1):

$$\hat{H} = -2J\Sigma\hat{S}_{\text{Co}i}S_{\text{Co}i+1} \qquad (1)$$

$$\chi = [Ng^2\beta^2S(S+1)]/(3kT)[(1+u)/(1-u)]$$
$$\chi_{\text{chain}} = \chi/[1 - zJ'\chi/(Ng^2\beta^2)] \qquad (2)$$

where $u(K) = \coth(K) - 1/K$, $K = 2JS(S+1)/kT$, and $S = {}^3/_2$; z is the number of neighbored chains, which is 2 in the present case; J' is the interchain exchange.

The fitting was performed with the susceptibility data above 34 K because of the effects of the spin−orbit coupling which are significant for Co(II) ions at lower temperature, and it gives magnetic parameters of $J = -3.52$ cm^{-1}, $J' = -0.29$ K $= -0.20$ cm^{-1}, and $g = 2.45$ and agreement factors of $R = 2.87 \times 10^{-5}$ [R is defined as $R = \Sigma(\chi_{\text{obsd}} - \chi_{\text{calcd}})^2/(\chi_{\text{obsd}})^2$]. The value $J = -3.52$ cm^{-1} indicates that there is an anti-ferromagnetic interaction between the bridged Co(II) ions which is compatible with the result of the calculations. However, comparing the J values that are from both the calculations and the fitting, respectively, it can be known that the J absolute value from the fitting is smaller than that of the calculation. The difference may arise from the following factors. First, the calculations indicate that both ferromagnetic interaction and anti-ferromagnetic interaction exist in the complex, and therefore, some anti-ferromagnetic interaction is certainly offset by the ferromagnetic interaction which leads to the decrease of the anti-ferromagnetic interaction. Second, the function employed in the density functional theory (DFT) calculation may overestimate the stability of the broken-symmetry state a bit and also lead to the large J absolute value of the calculations. Third, the fitting J value is from a model of a one-dimensional chain and was performed with the data above 34 K; the calculation comes from a binuclear model, whereas the true structure is a two-dimensional sheet. All of these factors may bring about some error. In addition, it is very normal that there is a certain error between calculation value and experimental value to data.[5,24]

The magnetic interaction intensity of the present complex is stronger than that ($J = -0.38$ cm^{-1}) of the complex[25] with pyrazine as a bridging ligand. The strong magnetic interaction may arise from the fact that the coordination O atoms of the *N*-oxide groups possess larger electronic density than that of the N atoms of the pyrazine ring,[26] and it also confirms again that the distance between bridging metal ions is not the sole decisive factor for the magnetic coupling intensity. The magnetic interaction intensity of the present complex is close to the complex with pyrazine-1,4-dioxide as a bridging ligand.[27]

Conclusions

In this work, a new two-dimensional polynuclear Co(II) complex has been synthesized with thiocyanate anion and 2,5-dimethylpyrazine-1,4-dioxide as mixed bridging ligands and its crystal structure determined. The theoretical calculations reveal that an anti-ferromagnetic coupling exists between the $\mu_{1,6}$-dmpzdo-bridged Co(II) ions and a ferromagnetic interaction exists between the $\mu_{1,3}$-SCN$^-$ bridging Co(II) ions, and the anti-ferromagnetic interaction is stronger than the ferromagnetic coupling. The experimental results confirm that there is anti-ferromagnetic interaction between the bridging Co(II) ions.

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Supporting Information Available: The X-ray crystallographic file of the title compound, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. This file has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 249998. A copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1Z, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; website, http://www.ccdc.cam.ac.uk).

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