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ANTI-FERROMAGNETIC EXCHANGE INTERACTION IN THE TETRACOBALT COMPLEX OF 2-MERCAPTOPYRIDINE-*N*-OXIDE (mpo), $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]Br \cdot DMF$

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Abstract—The exchange coupling of cobalt atoms in the mixed-valence tetracobalt complex with 2-mercaptopyridine-*N*-oxide (mpo) ligands, $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]Br \cdot DMF$, has been examined by fitting the variable-temperature magnetic susceptibility based on the Heisenberg theory. The results show that the complex exhibits anti-ferromagnetic coupling between Co^{II} and Co^{III} sites with a coupling constant J of -20.5 cm^{-1}. Uncertainty of the J value obtained is surveyed by an error analysis procedure.

The magnetic properties of cobalt complexes attracted the attention of chemists as early as the 1960s.[1–3] Due to its importance to magnetic materials as well as biologically active molecules, studies on the magnetism of Co^{II} complexes have been active for many years.[4–10] These studies can be summarized as considering three aspects: mononuclear Co^{II} complexes with tetrahedral ($S = 3/2$) or octahedral ($S = 1/2$) symmetries; ferromagnetically coupled two-dimensional Co^{II} chains; and model complexes for cobalt enzymes. This paper reports the magnetic properties of a tetracobalt complex with 2-mercaptopyridine-*N*-oxide (mpo) ligands, $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]Br \cdot DMF$.[11] Temperature-dependent magnetic susceptibility was measured and corresponding theories were developed to analyse the magnetic properties of the complex. The powder EPR spectrum was also recorded.

EXPERIMENTAL AND THEORY

Physical measurements

Variable-temperature magnetic susceptibility was measured on a Shimadzu MB-2 Magnetic Balance with the powdered sample kept in capsules for weighing. A magnetic field of 12 kOe was applied and maintained constant. The temperature of the sample was raised gradually from 70 to 300 K. Data were recorded in this temperature range at an applied field gradient $H\,\mathrm{d}H/\mathrm{d}x$ of 1.4×10^7 Oe^2 cm^{-1}. An interval of 30 s was maintained between data collection and each measurement took 10 s. The powder EPR experiment was carried out on a Bruker ER-420 spectrometer at room temperature.

Description of the structures

A chemical diagram of the cation $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]^+$ is given in Fig. 1.[11] The cation consists of four cobalt atoms in the form of a four-membered distorted square planar configuration with indirect metal–metal interaction, bridged symmetrically by two oxygen and three sodium atoms via the oxygen atoms of all mpo ligands. Each cobalt atom is coordinated by two bidentate mpo ligands with two different $S_tO_{b\text{-}D}$ and $S_tO_{b\text{-}T}$ (subscript t for terminal, b-D for bridging of two metal atoms and b-T for bridging of three metal atoms) coordination modes. Two $Co(mpo)_2$ units are bridged by (μ_3-O) to form $Co_2O(mpo)_4$ groups which, in addition, are structurally connected by three sodium atoms through the oxygen atoms of

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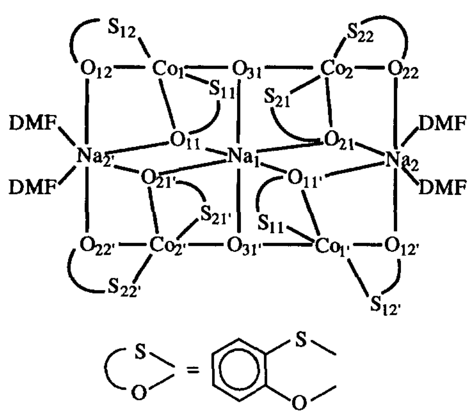

Fig. 1. Chemical diagram for the $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]^+$ cation.

the mpo ligands and the bridging μ_3-O, as shown in Fig. 1. The coordination sphere of Co(1) and Co(2) is approximately a distorted square pyramidal with two sulphur and two oxygen atoms from mpo ligands forming the basic square plane and one oxygen atom from μ_3-O in the apical position. The structure of the cation possesses a crystallographic inversion centre with the atom Na(1). The Co—Co separations fall into three types as $r_{Co(1)-Co(2)}$ 3.385 Å, $r_{Co(1)-Co(1)'}$, 6.811 Å and $r_{Co(1)-Co(2)'}$ 5.841 Å respectively. The X-ray diffraction analysis reveals that the complex contains essentially equivalent cobalt sites with a mean cobalt oxidation state of +2.5.

Theoretical model and computations

The simple isotropic Heisenberg model is applied to parameterize the exchange interaction in the complex and to simulate the variable-temperature susceptibility data. The Hamiltonian interaction can be expressed as:

$$\mathbf{H} = g\mu_B \sum_i H \cdot S_i - 2 \sum_{i<j} J_{ij} S_i \cdot S_j. \quad (1)$$

The first term gives the Zeeman interaction of the cobalt spins with the applied magnetic field H and the second term the isotropic exchange interaction; g is the electronic gyromagnetic ratio, μ_B the Bohr magneton and S_i the spin on the ith cobalt atom; J_{ij} is the exchange coupling constant between spins S_i and S_j. The sign of J_{ij} is positive for ferromagnetic and negative for anti-ferromagnetic spin coupling.

Based on the studies of the magnetic properties of mixed-valence complexes,[12,13] it can be assumed that each $Co_2O(mpo)_4$ group contains a Co^{II} and a Co^{III} site with localized spin $S = 1/2$ and $S = 1$, respectively. Compared with the interaction in each group of $Co_2(\mu_3\text{-}O)(mpo)_4$, the interactions between the two groups is negligible. The exchange coupling constant of each group is assumed to be J, while that between the two groups is assumed to be zero. The two groups can be treated separately and the total magnetic susceptibility of the molecule is a simple summation of the two components. Based on the Heisenberg–Dirac–Van Vleck theory, the temperature dependence of the molar susceptibility of a spin system containing $S_1 = 1/2$ and $S_2 = 1$ with an exchange coupling constant J can be derived[14] and the total molar susceptibility of the molecule can be expressed as:

$$\chi_M = 2 \cdot \left[\frac{Ng^2\mu_B^2}{4kT} \cdot \frac{10\exp(J/kT) + \exp(-2J/kT)}{2\exp(J/kT) + \exp(-2J/kT)} \right]. \quad (2)$$

Equation (2) contains two parameters, g and J, where g represents the average value of $g_{Co^{II}}$ and $g_{Co^{III}}$.

Based on eq. (2), a theoretical fitting of the experimental data of magnetic susceptibility can be carried out. The program QCP230, a non-linear fitting program from the Quantum Chemistry Program Exchange (QCPE) Center of the University of Indiana, has been modified to perform fitting of the magnetic susceptibility. Three parameters are included in the fitting, the g factor, the coupling constant J and a constant TIP added to the right side of eq. (2), where TIP represents the correction of all molar susceptibility values for the temperature-independent paramagnetism, as well as diamagnetism. Calculations were carried out using a VAX 11/785 computer with the VAX/VMS operation system. Inputting the non-linear theoretical formula with parameters, all the first- and second-order derivatives with respect to all the parameters, the experimental data, and the criterion for the square root of the theoretical and the experimental deviation, the program can produce values of all the parameters for the best fit of the theory to the experiment with an iteration procedure.

RESULTS AND DISCUSSION

The EPR spectrum depicted in Fig. 2 shows a broad line, which may indicate coupling between the cobalt atoms in the complex. With an SQRT criterion of 10^{-4}, the results obtained are given in Table 1. The variable-temperature magnetic susceptibility at 70–300 K is depicted in Fig. 3, where the effective magnetic moment per molecule is given as an inset. Figure 3 indicates an increase in effective magnetic moment with increasing temperature, which may correspond to the population of excited

Fig. 2. Powder ESR spectrum of $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]Br \cdot DMF$.

Table 1. Parameters obtained from fitting the variable-temperature susceptibility data of $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]^+$

g	J (cm^{-1})	TIP (cgsu)	$E_{1/2}$ (cm^{-1})	$E_{3/2}$ (cm^{-1})
2.2	−20.5	0.0025	−41.0	20.5

The energies of the two lowest excited states are also given.

states with spins higher than that of the ground state. Fitting results show that each part is anti-ferromagnetically coupled and the two magnetic parts are equivalent. Each part shows only two spin states, i.e. the $S_T = 1/2$ ground state and the $S_T = 3/2$ excited state, with an energy separation of 61.5 cm^{-1}. The spin system gains in population of the $S_T = 3/2$ excited state with increasing temperature and results in the increase of the effective magnetic moment.

Assuming distorted square pyramidal Co^{II} and Co^{III} in low spin states of $S = 1/2$ and $S = 1$, respectively, the parameters obtained are reasonable. This is the only theoretical model to account for the magnetic exchange interaction and produce correct magnetic behaviour of the complex.

The residual error (*Er*) of fitting expressed by eq. (3) can be applied to analyse the accuracy of the exchange parameter J obtained.[13]

$$Er = \frac{\sum_i [\chi_i(\text{exp}) - \chi_i(\text{calc})]}{\sum_i \chi_i(\text{exp})}. \qquad (3)$$

The behaviour of *Er* as a function of J is calculated according to eq. (3) and depicted in Fig. 4. There is a sharp minimum in *Er* vs J, which means that the parameters are well determined.

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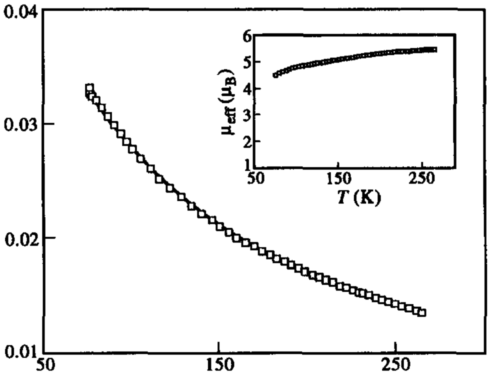

Fig. 3. Experimental and calculated temperature dependence of molar magnetic susceptibility per complex χ_M (cgsu) of $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]Br \cdot DMF$. The relationship of effective magnetic moment per complex vs T (K) is shown as an inset.

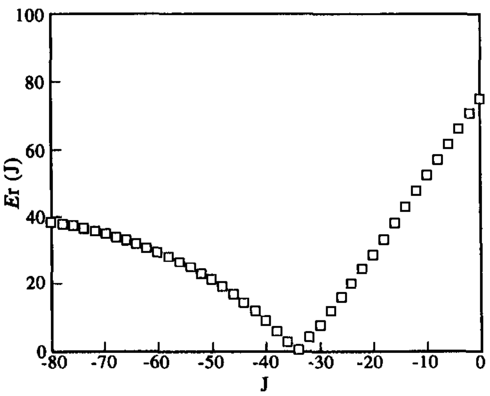

Fig. 4. Plot of the residual error of fitting, *Er*, vs the exchange parameter J for $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]Br \cdot DMF$.

Laboratory, Institute of Physics, Beijing, for measurement of the variable-temperature magnetic susceptibility.

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