Magnetic Properties of Diaquabis(phenoxyacetato)manganese(II) and Related Complexes

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The magnetic susceptibilities of diaquabis(phenoxyacetato)manganese(II), diaquabis(p-chlorophenoxyacetato)manganese(II), and diaquabis(phenoxyacetato)cobalt(II) were determined in a temperature region below 77 K. The temperature dependence of the magnetic susceptibility observed for the first two manganese(II) complexes shows a broad maximum near 2 K, which can be interpreted as arising from two-dimensional Heisenberg antiferromagnets with $S = 5/2$. The magnetic susceptibility of the cobalt(II) complex obeys the Curie-Weiss law showing the presence of a ferromagnetic interaction between neighboring cobalt(II) ions. For diaquabis(phenoxyacetato)manganese(II), a magnetic phase transition from a disordered to an antiferromagnetic ordered state was located at 1.633 ± 0.005 K from the sharp maximum of the magnetic susceptibility.

Introduction

According to Smith et al. [1], diaquabis(phenoxyacetato)manganese(II), $Mn(C_6H_5OCH_2CO_2)_2(H_2O)_2$, diaquabis(p-chlorophenoxyacetato)manganese(II), $Mn(p\text{-}ClC_6H_4OCH_2CO_2)_2(H_2O)_2$, and diaquabis(phenoxyacetato)cobalt(II), $Co(C_6H_5OCH_2CO_2)_2(H_2O)_2$, which are abbreviated as $Mn(phac)_2(aq)_2$, $Mn(p\text{-}Clphac)_2(aq)_2$, and $Co(phac)_2(aq)_2$, respectively, form orthorhombic crystals belonging to the space group $Pbca(D_{2h}^{15})$ with $Z = 4$. In the crystals, magnetic ions are bridged together by phenoxyacetato-ligands to form a two-dimensional network. As an example, the crystal structure of $Mn(phac)_2(aq)_2$ viewed down along the c-axis is schematically shown in Figure 1. Here, only an infinite layer $[Mn(phac)_2(aq)_2]_n$ spread out on an ab-plane at $c = 0$ is depicted. Another layer having analogous structure exists at $c = 1/2$. In each layer, every Mn(II) ion is octahedrally coordinated by six oxygen atoms, two from trans-related water molecules and four from phenoxyacetato-ligands. The principal molecular axis of the ligands lies approximately parallel to the c-axis. The Mn(II) ions in a layer are separated by 5.21 Å from one another, while the separation of two neighboring layers amounts to 16.6 Å. Accordingly, it is expected that the magnetism of these complexes can be interpreted in terms of two-dimensional magnetic systems [2].

The present investigation has been undertaken in order to obtain information on the magnetism of these complexes and also to examine the degree of the two-dimensionality in their magnetic properties.

Experimental

The three phenoxyacetato complexes studied were prepared according to the method described in the literature [1, 3], and identified by taking X-ray powder patterns. The cell parameters determined for each complex agreed well with those reported by Smith et al. [1].

An ac bridge operated at 150 Hz was employed below 20 K for the determination of the magnetic susceptibility of the pulverized samples [4]. In the

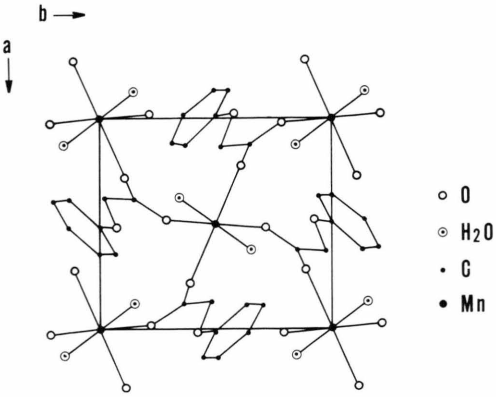

Fig. 1. Crystal structure of diaquabis(phenoxyacetato)-manganese(II) viewed down along the c-axis. A layer at $c = 0$ is shown.

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temperature range 20 – 77 K, the magnetic susceptibility was measured by the Faraday method. For the evaluation of the absolute value of the susceptibility, $CuSO_4 \cdot 5H_2O$ was used as a standard sample [5]. The observed molar susceptibility was not corrected for diamagnetic contributions throughout this paper, because extremely large values were obtained in the present study carried out at low temperatures. Sample temperatures below 4.2 K were determined by use of a germanium resistance thermometer, CR1000-1.5-100, calibrated at Cryocal Inc. A carbon resistance thermometer and an Au/Co versus Pt thermocouple, both of which were calibrated by measuring the magnetic susceptibility of $CuSO_4 \cdot 5H_2O$ [5], were used for the temperature determination in the temperature ranges 4.2 – 20 K and above 20 K, respectively. The accuracy of the observed temperature was estimated to be within ± 0.01 K below 4.2 K, ± 0.05 K between 4.2 and 10 K, ± 0.5 K between 10 and 20 K, and ± 2 K above 20 K.

X-ray powder patterns were taken at room temperature by means of an X-ray diffractometer, Model D-3F, from Rigaku Denki Co. equipped with a copper anticathode. The ESR spectra were recorded by use of a JEOL SCXA X-band spectrometer. As a standard for g-values, Mn^{2+}/MgO was employed.

Results

The magnetic susceptibilities of the two Mn(II) complexes determined at various temperatures below 4.2 K are plotted against the temperature in Figure 2. The susceptibility of both complexes decreased monotonously with increasing temperature above 4.2 K. A broad maximum at about 2.2 and 1.8 K was obtained for $Mn(phac)_2(aq)_2$ and $Mn(p\text{-}Clphac)_2(aq)_2$, respectively.

The susceptibility of the former complex shows another very sharp maximum at 1.63 K. To determine the remperature T_c where the susceptibility reaches the maximum value, the temperature dependence of the susceptibility was carefully measured by means of the ac bridge with its maximum field strength at about 1 Oe. This is one tenth of the field strength employed for usual measurements. The results are shown in Figure 3. For the precise determination of the sample temperature, the resistance R of the germanium resistance thermom-

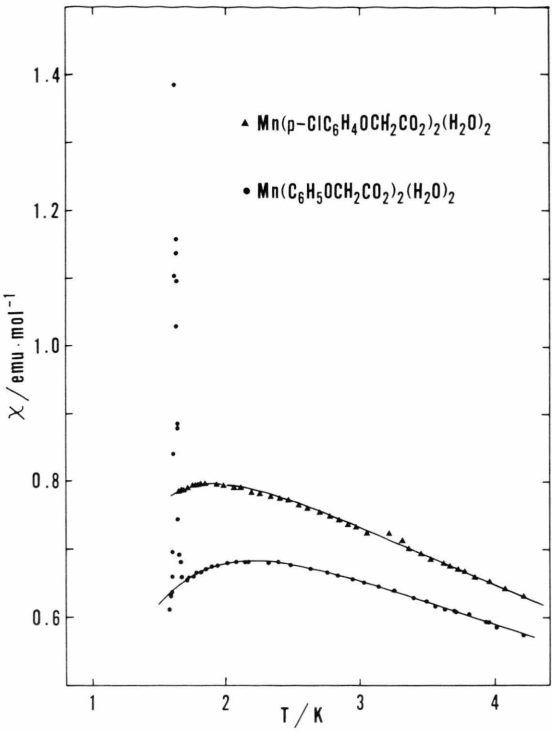


Fig. 2. Temperature dependence of the powder susceptibility of diaquabis(phenoxyacetato)manganese(II) and diaquabis(p-chlorophenoxyacetato)manganese(II). For each complex, the solid curve shows the best fit curve calculated by use of the high-temperature series expansion for the two-dimensional square-planar Heisenberg model with $S = 5/2$.

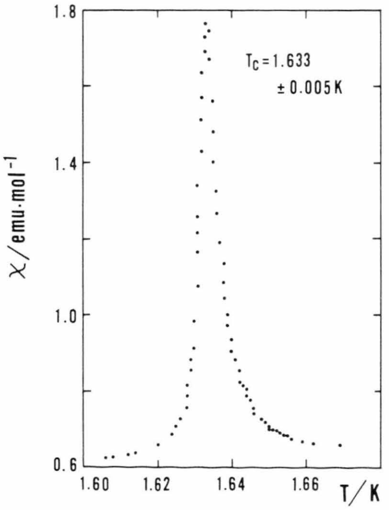


Fig. 3. Temperature dependence of the susceptibility of diaquabis(phenoxyacetato)manganese(II) near T_c.

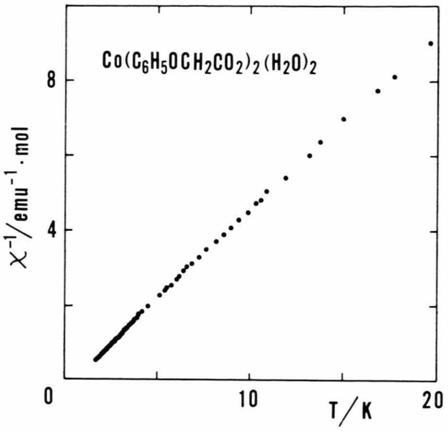


Fig. 4. Temperature dependence of the inverse susceptibility of diaquabis(phenoxyacetato)cobalt(II).

eter expressed as a function of the temperature T was fitted to the following empirical formula [6]:

$$\log_{10} R = \sum_{n=1}^{14} A_n (\ln T)^{n-1}\,, \qquad (1)$$

using 35 calibration data determined between 1.50 and 20 K at Cryocal Inc. The fitting calculation was performed at the computation ceter of Nagoya University by use of the least squares computer program SALS [7]. Employing this empirical formula, T_c was determined as (1.633 ± 0.005) K.

The reciprocal susceptibility $1/\chi$ of the Co(II) complex determined at various temperatures below 20 K is plotted in Figure 4.

Discussion

The broad maximum of the susceptibility versus temperature curve observed for our Mn(II) complexes is characteristic of low-dimensional magnetic systems with an antiferromagnetic coupling between neighboring magnetic ions [2]. Since there exists a two-dimensional network of the magnetic Mn(II) ions in the crystal of these complexes, the two-dimensional model seems to be adequate for the low-dimensional magnetic system. Assuming the high-spin state with $S = 5/2$ for the Mn(II) ions having a vanishing orbital angular momentum contribution, the two-dimensional Heisenberg model was employed for the interpretation of the susceptibility of the Mn(II) complexes observed.

When only the nearest-neighbor interaction is taken into account, the high-temperature series expansion for the susceptibility χ is given by

$$\chi = \frac{N g^2 \mu_B^2 S(S+1)}{3kT}\left[\sum_{n=0}^{\infty} b_n (J/kT)^n\right]^{-1}. \qquad (2)$$

Here, apart from obvious notations, J is the exchange integral between the nearest-neighbor Mn(II) ions. For the two-dimensional square-planar Heisenberg model with $S = 5/2$, the coefficients b_n in (2) are given as [8, 9], $b_0 = 1$, $b_1 = -23.33333$, $b_2 = 147.7778$, $b_3 = -405.4815$, $b_4 = 8171.312$, $b_5 = -64967.81$, $b_6 = 158110.0$, and $b_7 = -461192.6$.

Neglecting terms with $n \geqq 8$, the fit of the susceptibility values obtained below 4.2 K to the high-temperature series expansion for the two-dimensional square-planar Heisenberg model was examined by use of the computer program SALS [7]. In the calculation, the Curie constant

$$C = N g^2 \mu_B^2 S(S+1)/3k\,, \qquad (3)$$

and the exchange integral J were varied as numerical parameters. The best fit of the theoretical curve to the observed values of the susceptibility was obtained (Fig. 2) with $C = 4.42$ emu K mol^{-1} and $J/K = -0.12$ K for $Mn(phac)_2(aq)_2$ and $C = 4.52$ emu K mol^{-1} and $J/K = -0.11$ K for $Mn(p\text{-}Clphac)_2(aq)_2$.

The g-values calculated from the above Curie constants are 2.01 and 2.03 for the former and the latter complex, respectively. The powder ESR measurements of these complexes gave isotropic spectra with a g-value of 2.02 and a maximum slope linewidth of about 125 Oe for both complexes at room temperature. The g-value directly observed by ESR is in good agreement with that calculated from the Curie constant assuming $S = 5/2$, indicating that the Mn(II) ions of these complexes are undoubtedly in the high-spin state. The agreement of the theoretical curves (solid curves in Fig. 2) with the experimental susceptibility data is excellent in a fairly wide range of temperature below 77 K, although only the data below 4.2 K are given in Figure 2. This excellent agreement indicates that the magnetism of both Mn(II) complexes is well described as a two-dimensional Heisenberg antiferromagnet with $S = 5/2$.

The sharp maximum of the observed susceptibility versus temperature curve of $Mn(phac)_2(aq)_2$

can be attributed to a weak ferromagnetism [10], indicating the occurrence of a magnetic phase transition at T_c and the presence of a three-dimensionally ordered spin state below T_c. Although Mn(p-Clphac)$_2$(aq)$_2$ is expected to undergo a similar phase transition, no anomaly of the susceptibility was observed down to 1.65 K, which was the lowest temperature reached with this complex. For the magnetic phase transition of the pseudo two-dimensional magnets, there exists a tendency that the T_c values are practically independent of the interlayer distances when the interlayer spacing exceeds 15 Å [9]. However, it becomes obvious from the detailed investigation of the available data for $(C_nH_{2n+1}NH_3)_2CuCl_4$ and $(4\text{-}XC_6H_4NH_3)_2MnCl_4$ [2, 9] that T_c slightly decreases with decreasing absolute magnitude of the J values. In the present Mn(II) complexes having longer interlayer separations, Mn(p-Clphac)$_2$(aq)$_2$ has a smaller $|J|$ value than Mn(phac)$_2$(aq)$_2$, suggesting that the phase transition expected for the former complex may occur at a lower temperature.

The values of J/k obtained for both Mn(II) complexes along with those of related compounds which are known as the two-dimensional Heisenberg antiferromagnets are shown in Table 1. The present Mn(II) complexes give smaller $|J/k|$ values than that of $Mn(HCOO)_2 \cdot 2H_2O$ [11], which is known as the typical example of a two-dimensional Heisenberg antiferromagnet with $S = 5/2$ among those complexes having carboxylato groups as a bidentate ligand bridging neighboring Mn(II) ions. Although T_c of Mn(phac)$_2$(aq)$_2$ is lowest among the Mn(II) complexes listed in Table 1, the ratio of $kT_c/|J|$, which can be employed as a measure of deviations from the ideal two-dimensional magnet [2], is largest. This suggests that Mn(phac)$_2$(aq)$_2$ is rather unsuitable as a good example of a model compound of a two-dimensional Heisenberg antiferromagnet.

The magnetism of Co(phac)$_2$(aq)$_2$ is quite different from that of the foregoing Mn(II) complexes. As shown in Figure 4, the susceptibility observed below about 20 K obeys the Curie-Weiss law,

$$\chi^{-1} = (T - \theta)/C \tag{4}$$

with the Curie constant $C = 2.06$ emu K mol^{-1} and the Weiss constant $\theta = 0.6$ K. The positive Weiss constant indicates the predominance of ferromagnetic interaction in the crystal.

The effective magnetic moment μ_{eff} is defined as

$$\mu_{\text{eff}} = (3kC/N)^{1/2}, \tag{5}$$

where N denotes Avogadro's number. For the Co(II) complex, μ_{eff} was calculated to be 4.06 μ_B. If the magnetic moment is determined only by the moment of the electron spins, μ_{eff} should be equal to 1.73 and 3.88 μ_B for a Co(II) ion having the low-spin state with $S = 1/2$ and the high-spin state with $S = 3/2$, respectively. Since the observed moment is very close to the spin-only value of Co(II) with $S = 3/2$, the high-spin state is more plausible for the electronic structure of the Co(II) ion of this complex. However, the effective spin formalism with $\hat{S} = 1/2$ should be employed for the analysis of the susceptibility data obtained at relatively low temperatures, because the lowest electronic state of a Co(II) ion having $S = 3/2$ becomes a doublet by introducing the spin-orbit coupling [14]. Assuming $\hat{S} = 1/2$, the averaged g-value was estimated to be 4.69 from the Curie constant evaluated above. Unfortunately, we could not confirm the adequacy of the g-value because no ESR spectrum was observed on the powder sample at room temperature. This suggests that the Co(II) ion has high

Table 1. The phase transition temperature T_c, the exchange integral J, and the ratio of $kT_c/|J|$ observed for some quadratic layer antiferromagnets of manganese(II) compounds.

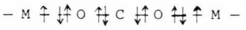
Compound	(Ref.)	T_c/K	(J/k)/K	$kT_c/\|J\|$
$Mn(p\text{-}ClC_6H_4OCH_2CO_2)_2(H_2O)_2$		–	−0.11	–
$Mn(C_6H_5OCH_2CO_2)_2(H_2O)_2$		1.633	−0.12	13.6
$Mn(trz)_2(NCS)_2$[a]	[13]	3.29	−0.25	13.1
$Mn(C_2H_5OH)_2(NCS)_2$	[12]	10.30	−0.88	11.7
$Mn(HCOO)_2 \cdot 2H_2O$	[11]	3.68	−0.34	10.8

[a] trz = 1,2,4-triazole.

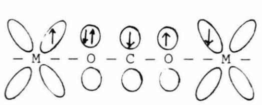
anisotropy of its electronic state [14] resulting from the cation in a lower-symmetry crystalline field than cubic.

In the crystals of the present complexes, there exist carboxylato groups, each of which connects two neighboring magnetic ions by coordination bonds. Roughly speaking, two different paths of the superexchange interaction through carboxylato groups, (I) and (II) indicated below, are conceivable in this case for the transfer of electron-spin polarization.

(I)



(II)



Unpaired electron spins generated in the e_g and t_{2g} orbitals of the metal ions are mainly involved in the σ path (I) and the π path (II), respectively. The exchange interaction through the σ path causes a ferromagnetic coupling between two unpaired spins situated on neighboring metal ions, while the interaction through the π path operates antiferromagnetically.

The Mn(II) and Co(II) ions in the high-spin state possess three and one unpaired electron, respectively, in their t_{2g} orbital, while they have two unpaired electrons in their e_g. Therefore, the exchange interaction through the π path is considered to be less important for Co(phac)$_2$(aq)$_2$ as compared with the Mn(II) complexes investigated, because the number of unpaired electrons in the t_{2g} orbital is smaller for Co(II) ion than in the Mn(II) ion. This may be one of the reason why the superexchange interaction is ferromagnetic and antiferromagnetic for the present Co(II) and Mn(II) complexes, respectively. Although the above explanation of the exchange interaction is rather qualitative, the same conclusion will be derived from a more quantitative discussion using the recent orbital models proposed by Kahn and Briet [15].

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