Dielectric Behavior of Manganese(III) Spin-Crossover Complex [Mn(taa)]

Motohiro Nakano* and Gen-etsu Matsubayashi†
Department of Molecular Chemistry & Frontier Research Center,
Graduate School of Engineering, Osaka University, Toyonaka, Osaka 560-0043, Japan

Takasuke Matsuo‡
Department of Chemistry & Research Center for Molecular Thermodynamics,
Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan
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Paraelectric behavior due to a dynamic Jahn-Teller (JT) effect is reported for the manganese(III) spin-crossover complex [Mn(taa)] (H₃taa = tris(1-(2-azolyl)-2-azabuten-4-yl)amine) in the high-spin (HS) phase above $T_c = 48$ K. The dielectric constant obeys the Curie-Weiss law with an asymptotic Curie temperature 26 K, suggesting competition between a low-spin (LS) phase and a ferrodistortively-ordered (FO) phase at low temperatures. A phase diagram based on a 4-state Ising-Potts model incorporating both a virtual cooperative JT transition (HS→FO) and a spin-crossover transition (HS→LS) is proposed to elucidate the interrelation of the HS, LS, and FO phases.

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A number of octahedral transition metal complexes possessing four to seven $d$-electrons are known to show a molecular bistability of electron configurations, i.e. the high-spin (HS) and low-spin (LS) states distinguished by different occupation of $e_g$ and $t_{2g}$ orbitals in the complex. The electronic ground state of such complexes may interchange one to the other under certain molecular deformations, especially a totally-symmetric breathing mode, and these phenomena are called spin crossover. In thermally driven spin-crossover phenomena, stable LS states are populated at low temperatures and entropically favored HS states become dominant at higher temperatures. In general, the entropy difference between LS and HS states, which is responsible for the thermally driven transition, does not come solely from the change in spin degeneracy, but also from the vibrational entropy related to the softening of breathing mode molecular vibrations. This observation, in fact, plays a role of the central dogma for thermally driven spin-crossover phenomena, and has been repeatedly confirmed by far-IR, laser Raman, and INS spectroscopies.

The title compound, [Mn(taa)] (H₃taa = tris(1-(2-azolyl)-2-azabuten-4-yl)amine) in the cubic crystalline form is known to exhibit an abrupt $^5E \leftrightarrow ^3T_1$ spin-crossover phase transition at 48 K. The calorimetric study on the compound reported the transition entropy of 13.8 J K$^{-1}$mol$^{-1}$, of which only one third has been explained by spin multiplicities, and this apparently supports that the complex [Mn(taa)] shows an ordinary spin-crossover transition assisted by vibrational entropy. Our recent work, however, revealed that most of the Raman-active vibrational modes are nearly independent of the spin states. It strongly suggests that an entropy source alternative to vibrational one should be involved in the spin-crossover transition of [Mn(taa)]. In this Communication, we present dielectric data on [Mn(taa)], which indicates the presence of dynamic disorder responsible for the excess entropy in the HS phase.

Molecular structure of [Mn(taa)] is schematically shown in FIG. 1. It has a C₃ symmetry axis through the Mn and non-ligating N atoms. The other six N atoms complete a trigonal-antiprismatic (distorted octahedral) coordination to the central Mn atom with right-handed or left-handed helicity. However, C₃ symmetry of the molecule imposed by the crystallographic space group $I43d$ is not compatible with the Mn(III) ion in the $^5E$ state, since it is a typical Jahn-Teller (JT) ion and its orbital degeneracy cannot be lifted by trigonal distortion. Thus the dynamic disorder between $E \otimes e$ JT-deformed configurations is plausible at room temperature where the crystal structure was resolved.

Adiabatic potential surfaces of a $d^4$ spin-crossover system are depicted in FIG. 2. The $E \otimes e$ JT effect gives rise to three minima on the HS state $^5E$ ($S = 2$) over doubly degenerate interaction mode $(q_1, q_2)^{12}$. These minima correspond to stretched-octahedron molecular configurations of HS species with one of three N-Mn-N coordination axes elongated. On the other hand, the LS...
state $^3T_1$ ($S = 1$) has a surviving orbital angular momentum and the spin-orbit interaction and trigonal distortion completely lifts the orbital degeneracy without symmetry lowering to provide a totally symmetric $^3A$ state as the ground level.

The three-fold disorder corresponding to the three minima on the $^5E$ surface in FIG. 2 will contribute reorientational entropy of $\Delta S_{\text{JT}} = R \ln 3$ to the HS species. With this degrees of freedom taken into account, the transition entropy from the $^3A$ LS state to the dynamic JT state will be equal to $\Delta S = \Delta S_{\text{mag}} + \Delta S_{\text{JT}} = R \ln(5/3) + R \ln 3 = 13.4 \text{ J K}^{-1}\text{mol}^{-1}$, which agrees well with the experimental value\textsuperscript{10}. If dynamic JT distortion occurs, the distorted molecule will carry a reorienting electric polarization, because of the low local symmetry of the Mn(III) site, while there will be no such dielectric response in the $^3A$ LS state.

A polycrystalline sample of [Mn(taa)] was prepared according to the literature\textsuperscript{10}. Dielectric constants were measured on a compacted pellet with vacuum-deposited Au electrodes by using a precision LCR meter (Hewlett-Packard 4282A) in a frequency range $10^2$-$10^6$ Hz and a temperature range 15-300 K. The sample disk was 0.55 mm thick and 12 mm in diameter. The evaporated Au electrodes were 9.0 mm in diameter. The sample was mounted on a copper addendum equipped with an electrical heater and an Rh-Fe resistance thermometer calibrated against the ITS-90. The sample assembly was placed in a thermostated He atmosphere ($\approx 10^4$ Pa).

Temperature dependence of the dielectric constant of [Mn(taa)] measured at 1.0 kHz is shown in FIG. 3. Remarkable imaginary components and/or frequency dependence characteristic of dielectric relaxations were not observed. A large gap accompanying with the spin-crossover transition at 48 K was found, above which the dielectric constant obeys the Curie-Weiss law $C/(T - \theta)$ with an asymptotic Curie temperature $\theta$ of 26 K. The Curie constant $C$ of 91 K corresponds to a microscopic dipole moment of 1.25 D reorienting in the HS phase, where the cubic cell volume 8.377 nm$^3$ and $Z = 16$ are used. The Curie-Weiss behavior is fully suppressed in the LS phase. These observations are clear evidence of dynamic JT nature of the $^5E_g$ HS species with thermally-switching elongated N-Mn-N axes. The small dipole moment is consistent with the transverse molecular dipole of 0.88 D estimated for the JT-distorted HS species based on a hybrid DFT calculation (UB3PW91/LANL2DZ)\textsuperscript{13}. Of course, the transverse molecular dipole is zero in a LS species with the C$_3$ molecular symmetry.

Gradual growth of the $\epsilon'$ values in the temperature region 15-40 K corresponds to a thermal excitation process from the LS to HS state embedded in LS species. Assuming the temperature dependence of the form $T^{-1}\exp(-\Delta_{\text{eff}}/k_B T)$ for the dielectric constant\textsuperscript{14,15}, $\Delta_{\text{eff}}/k_B = 340$ K was found for the effective LS-HS energy gap in the LS phase. This value is much larger than the transition enthalpy $\Delta H$ since the gap is enhanced by intermolecular interactions between the LS and HS species.

The positive $\theta$ suggests the presence of intermolecular interactions between HS species bringing about a ferrodistortively-ordered (FO) phase \textit{via} a cooperative JT transition. Examining the Lorentz field on a molecular dipole embedded in the cubic lattice with high-frequency component $\epsilon_\infty \approx 3$, about 40 % of the intermolecular interaction is attributable to the electrostatic origin. Although the FO phase is not actually observed because the LS phase forestalls the ordered JT state, a metastable FO phase may be realized \textit{via} a cooperative JT transition from a supercooled HS phase if the first-
order spin-crossover transition is circumvented by a rapid refrigeration.

A 4-state Ising-Potts model\textsuperscript{16} was examined under a mean-field approximation\textsuperscript{17} to describe an extended phase diagram incorporating the HS, LS, and FO phases. The internal energy is expressed by using the population \( \rho_0 \) of the LS species and populations \( \rho_1 \), \( \rho_2 \), and \( \rho_3 \) of the HS species elongated along the three axes:

\[
U = J_0 (\rho_1^2 + \rho_2^2 + \rho_3^2) + 2J_1 \rho_0 (\rho_1 + \rho_2 + \rho_3) + \Delta (\rho_1 + \rho_2 + \rho_3),
\]

where \( J_0 \) < 0 stands for the Potts-type ferrodistortive interaction between HS species, \( J_1 > 0 \) is the Ising-type demixing interaction between HS and LS species, and \( \Delta > 0 \) is the LS-HS gap. Although \( J_0 \) owes its large part to the electrostatic dipole-dipole interaction, both \( J_0 \) and \( J_1 \) include dominant contributions from the van der Waals interaction, especially \( J_1 \) comes from packing mismatch of neighboring HS and LS species. The phenomenological free energy \( F = U - T S \) is given by combining \( U \) with the entropy term:

\[
S = \rho_0 R \ln 3 + (1 - \rho_0) R \ln 5 - R \sum_{i=0}^{3} \rho_i \ln \rho_i.
\]

Equilibrium populations at temperature \( T \) are determined by minimizing this free energy under normalization condition, \( \rho_0 + \rho_1 + \rho_2 + \rho_3 = 1 \). The \( T-J_0 \) phase diagram thus calculated is plotted in FIG. 4: the HS region is the paraelectric phase where the LS species with \( C_3 \) molecular symmetry and three equivalent HS species coexist, the LS region is occupied by energetically stable LS species, and the FO region is the ferrodistortive phase ordered via a second-order cooperative JT phase transition of HS species.

Interaction parameters relevant to \([\text{Mn(taa)}]\) were determined to be \( J_0/k_B = -36 \text{ K} \), \( J_1/k_B = 125 \text{ K} \), and \( \Delta/k_B = 90 \text{ K} \), so as to reproduce the spin-crossover transition temperature \( T_c = 48 \text{ K} \), the virtual JT transition temperature \( T_{JT} \approx \theta = 26 \text{ K} \), and the effective LS-HS gap \( \Delta_{\text{eff}}/k_B = 340 \text{ K} \). (Under the mean-field approximation the effective gap \( \Delta_{\text{eff}} \) enhanced by the demixing interaction \( J_1 \) is approximated as \( \Delta + 2J_1 \).) The choice of the interaction parameters provides the transition enthalpy \( \Delta H = 0.64 \text{ kJ mol}^{-1} \) and the transition entropy \( \Delta S = 13.3 \text{ J K}^{-1} \text{ mol}^{-1} \) (FIG. 5), in satisfactory agreement with observed thermodynamic quantities\textsuperscript{10}. This fact strongly supports applicability of such a mean-field treatment to interpret the competing phase behavior in \([\text{Mn(taa)}]\).

The calculation presented here shows that main features of the spin-crossover transition in \([\text{Mn(taa)}]\) are described satisfactorily without invoking the participation of vibrational degrees of freedom. In particular, the transition entropy is fully explained in terms of the spin multiplicity and JT configurations. This is in distinct contrast to most of the other spin-crossover systems where softening of optical phonons is an important ingredient of the transition mechanism. This may be probably related with the coordination structure of \([\text{Mn(taa)}]\) in which all the six N atoms are concatenated through covalent bonds to form a rigid shell encapsulating the Mn(III) ion. Thus the rigid shell will accommodate only a minor JT deformation carrying the small transverse dipole moment 1.25 D, but will not allow softening of the Mn-N bond to take place in the HS state of \([\text{Mn(taa)}]\). The low-temperature Raman data of this complex\textsuperscript{11} seem to support this interpretation. It is also interesting that the HS and LS phases described by the free energy expressions given above have the same symmetry. Thus the phase transition may be an isomorphous transition\textsuperscript{18}. Determination of the crystal structure is desirable for the low-temperature phase.

In an iron(II) spin-crossover system \([\text{Fe(2-pic)}_3\text{Cl}_2 \cdot \text{EtOH}} (2\text{-pic} = 2\text{-aminoethylpyridine}), a metastable light-induced JT phase was reported\textsuperscript{19,20}. This situation is quite analogous to the present case, and it is a promising possibility that \([\text{Mn(taa)}]\) may also provide a metastable light-induced FO phase by UV/Vis irradiation below the virtual JT transition temperature \( T_{JT} = 26 \text{ K} \).

Dielectric measurements on the Mn(III) spin-crossover complex \([\text{Mn(taa)}]\) shed, for the first time, light on the presence of reorientating electric dipole moments in the HS phase and its full quenching in the LS phase. This
paraelectric behavior of the HS species is understood by considering a comprehensive free energy involving the dynamic JT effect and ferrodistortive interaction. A virtual cooperative JT transition into an FO phase was located in the extended phase diagram. By introducing additional control parameters, such as light irradiation\textsuperscript{19,20} and geometrical confinement\textsuperscript{21,22}, the assumed FO phase is likely to be observed in the present complex.

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\*moto@ch.wani.osaka-u.ac.jp
\†matsu@ch.wani.osaka-u.ac.jp
\‡matsuo@chem.sci.osaka-u.ac.jp

Figure 1
Figure 2
Figure 3
Figure 4
Figure 5