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ノート

Analogy of van't Hoff Relationship for Thermally-Accessible Lattice Strain of Copper(II) Complex

Takashiro Akitsu* and Kenji Sano

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In analogy with the mathematical form of thermodynamic van't Hoff equation ($\ln K = -\Delta H/RT + \Delta S/R$) for equilibrium systems, we proposed a similar relationship for thermally-accessible lattice strain of a certain copper(II) complex exhibiting anisotropic distortion. For this purpose we assumed that the degree of lattice strain plays a similar role to the equilibrium constant in the van't Hoff equation. We tested some predominant peaks of XRD patterns in the temperature range of 100 - 300 K. We found that the temperature dependence of the degree of the lattice strain was consistent with our assumption. Deviation from reasonable results was attributed to the treatment of isotropic *d*-values and characteristics requested by the crystal symmetry.

Keywords: X-ray diffraction, crystal, lattice, copper(II), thermally-accessible lattice strain

1. Introduction

In the field of coordination chemistry in the solid states, structural phase transition and spin transition (spin crossover) exhibiting bistability have been so far investigated thermodynamically.[1)] As one of structural phase transitions, copper(II) Tutton salts, general formula $A_2[Cu(H_2O)_6]B_2$, was studied with various experimental methods of crystallography. Recently, Schultz *et al.*[2)] reported dimorph showing hysteresis by applying various pressure and temperature in measuring neutron diffraction, and they found leaping lattice parameters at the phase transition temperature, whose thermodynamical parameters were evaluated based on Clapeyron equation ($dP/dT = \Delta H/T\Delta V$).

On the other hand, we have studied on cyanide-bridged bimetallic assemblies containing copper(II) moieties.[3)] Generally these complexes do not exhibit structural phase transition changing space group symmetry. Continuous structural changes thermally-accessible lattice strain (or negative thermal expansion[4,5)]) and Jahn-Teller distortion (if any switching elongation or contraction of axial coordination bonds[6)]) are also important phenomena for their electronic functions. For example, a picture of two states, such as 100 % Jahn-Teller distorted state at 0 K and 0 % Jahn-Teller distorted state at high temperature, can be considered for crystal states at arbitrary temperature. However, useful indices with physical meaning for thermally-accessible structural changes are limited so far.

Herein, in analogy with mathematical forms of thermodynamic van't Hoff equation ($\ln K = -\Delta H/RT + \Delta S/R$) for equilibrium systems to evaluate enthalpy and entropy from spectroscopic data,[7-12)] we attempted to apply similar relationship to thermally-accessible lattice strain of a certain copper(II) complex. Main goal of the present assumption is to judge normal or abnormal structural changes by varying temperature.

2. Experimental Section

Preparation, characterizations, crystal structure of the sample, $[CuL_2][Ag(CN)_2]_2 \cdot 3H_2O$ (L = (1*S*, 2*S*)-1,2-diaminocyclohexane), have been reported originally elsewhere.[13)] CCDC 734022: $C_{16}H_{36}Ag_2CuN_8O_4$, Monoclinic, $P2_1$, a = 11.5954(17) Å, b = 6.8668(10) Å, c = 16.956(3) Å, β = 108.490(2)°, and V = 1280.4(3)

Å^3, and $Z = 2$, $M = 675.75$, $D_c = 1.753$ Mgm^{-3}, $\mu = 2.372$ mm^{-1}, $R_1 = 0.0503$, $wR_2 = 0.1211$ (4999 reflections), $S = 1.172$, $T = 100(2)$ K, Flack parameter = 0.07(3).

Powder XRD patterns were measured by using synchrotron radiation at KEK-PF BL-8B (2008B526) with 8 keV radiation ($\lambda = 1.54184$ Å) in the 100-300 K temperature region.

3. Results and Discussion

In order to evaluate distinctly, we picked up XRD data measured at T = 100, 130, 150, 170, 190, 210, 230, 250, 270, and 300 K and focused on intense peaks around 10.4, 11.3, and 13.9° of a low-angle region (**Fig.1**). The peaks can be assigned to be Miller indices (100), (101), and (011) faces, respectively, by the single-crystal structural data. The direction vectors of Cu1-N1 (Jahn-Teller elongated axial bond) and Ag2-Ag1 (Ag ions of counter anion and axial ligand) are [0.22357, 0.02717, -0.47993] and [0.04098, 0.50883, -0.00092], respectively, which are apart from the *a*-axis [1, 0, 0], *b*-axis [0, 1, 0], and *c*-axis [0, 0, 1] in monoclinic coordinate systems.

At first, we converted diffraction angle of each peak into *d*-values according to Bragg equation:

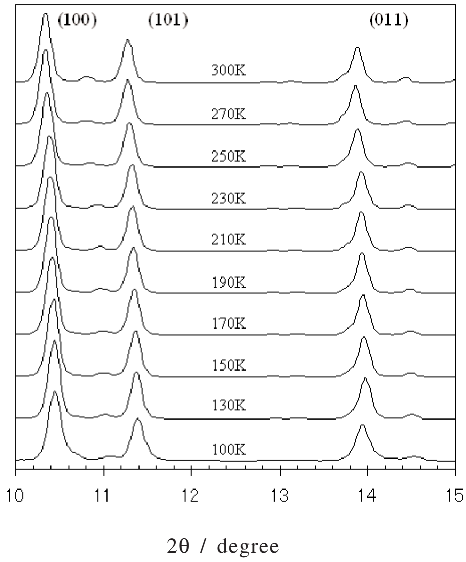


Fig.1 Temperature dependence of predominant (100), (101), and (011) peaks of XRD patterns with λ = 1.54184 Å radiation.

$$2d\sin\theta = \lambda \qquad (1)$$

Because of the complicated composition, we failed to determine lattice parameters by *ab-initio* methods regardless of clear powder XRD patterns. Since the crystal system is not tetragonal but monoclinic (nonsymmetric space group $P2_1$ requested by chirality), *d*-values are reduced to isotropic ones and do not correspond to each length of the *a*, *b*, and *c*-axes straightforwardly. The extrapolation of the *d* vs *T* plots gave rise to *d*-values at 0 K to be 8.407, 7.710, and 6.310 Å for the peaks of (100), (101), and (011) peaks, respectively.

We defined dimensionless *K* values at *T* instead of common equilibrium constants by law of mass action as follows:

$$K = [\mathrm{d}(T) - \mathrm{d}\ (0\ \mathrm{K})]\ /\ \mathrm{d}(T) \qquad (2)$$

considering degree of thermal expansion at *T* against ideal length of lattice at 0 K. This definition for the *K* values may be meaningless thermodynamically and mathematical formula to express structural changes phenomenologically. Actually, structural aspects of the complex may dominate both vibrational and electronic potential curves (so-called Mexican hat potential for Jahn-Teller effect$^{14)}$) and various natures of crystalline state and aggregations.

After accepting this assumption about the *K* values, we made ln*K* vs 1/*T* plots for ten data of the three series of peaks (**Fig.2**) to fit them to the following van't Hoff equation,

$$\ln K = -\Delta H/RT + \Delta S/R \qquad (3)$$

where the slope ($-\Delta H/R$) and the intercept ($\Delta S/R$) provide pseudo-enthalpy and pseudo-entropy terms, respectively. The resulting coefficients are $\Delta H/R = 176$ and $\Delta S/R = -3.53$ with decision coefficient of regression lines by least-squares fitting $D^2 = 0.99$ for (100) series, $\Delta H/R = 150$ and $\Delta S/R = -3.67$ with $D^2 = 0.89$ for (101) series, and $\Delta H/R = 121$ and $\Delta S/R = -4.34$ with $D^2 = 0.43$ for (011) series, respectively.

As for distortion of crystal lattice, when one assumes two states of high-temperature distributed length at *T* K and ideal length at 0 K (standard), the well-fitting *K* value (it is not defined as a simple $\Delta d/d$ form) presents the ratio of length of two states. Common temperature dependence of cell volume, $\Delta V/V = \beta\Delta T$ or rearranged

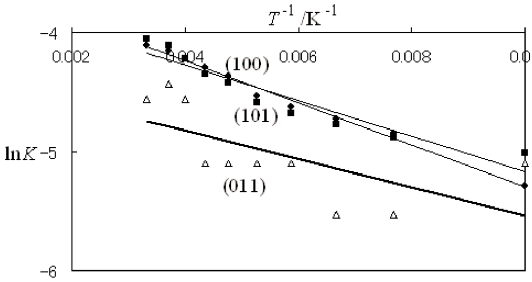


Fig.2 The ln K vs 1/T plot for (100) (filled circles), (101) (filled squares), and (011) (empty triangles) peaks. Fitting lines are also indicated.

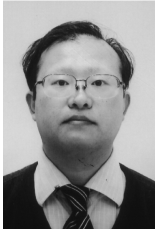
$\beta = \Delta V/(V\Delta T)$, obeys linear relationship affording possible states and providing constant β (> 0) value. Therefore, distinct difference between diffraction peaks exhibiting smooth expansion and possessing other factors or reasons for non-smooth expansion can be expected for the temperature dependent states of possible lattice lengths in this framework.

4. Concluding Remarks

Among the three (100), (101), and (011) series, most significant variation with small D^2 values (large deviation from the regression line) arises for (011) series, reflecting large shift of 2θ values by changing temperature. It may be ascribed to isotropic reduction employing d-values, otherwise essential anisotropic thermally-accessible distortion, which may be also supported by successful features for the specific Miller indices (100) and (101). Anyway the ln$K$ vs 1/T plots may be useful for finding smoothly structural changes for continuous expansion without phase transition by changing temperature. As for the present system, anisotropy of monoclinic systems may prevent from varying peak shift smoothly. Furthermore, anisotropic lattice strain with the *a*-, *b*-, and *c*-axes, relationship between crystal lattices formed by emitting heat of formation and thermodynamically conformational changes of flexible molecules as components, and abnormal behavior, for example negative thermal expansion, should be considered with more sophisticated treatment linked to thermodynamic or physical meanings distinctly.

References

1) For example, M. Sorai, M. Nakano, and Y. Miyazaki, *Chem. Rev.* **106**, 976 (2006) and references therein.
2) A. J. Schultz, R. W. Henning, M. A. Hitchman, and H. Stratemeier, *Cryst. Growth Des.* **3**, 403 (2003).
3) T. Akitsu, *J. Cryst. Soc. Jpn.* **50**, 201 (2008) and references therein (in Japanese).
4) J. S. O. Evans, *J. Chem. Soc., Dalton Trans.* 3317 (1999).
5) L. R. Falvello, *J. Chem. Soc., Dalton Trans.* 4463 (1997).
6) M. A. Halcrow, *Dalton Trans.* 4375 (2003).
7) M. R. Guzzo, M. Uemi, P. M. Donate, S. Nikolaou, A. E. H. Machado, and L. T. Okano, *J. Phys. Chem. A* **110**, 10545 (2006).
8) J. He, A. G. Petrovic, and P. L. Polavarapu, *J. Phys. Chem. B* **108**, 20451 (2004).
9) N. Svanvik, J. Nygren, G. Westman, and M. Kubista, *J. Am. Chem. Soc.* **123**, 803 (2001).
10) A. Niedzwiecka, E. Darzynkiewicz, and R. Stolarski, *Biochemistry* **43**, 13305 (2004).
11) M. Miguirditchian, D. Guillaneux, D. Guillaumont, P. Moisy, C. Madic, M. P. Jensen, and K. L. Nash, *Inorg. Chem.* **44**, 1404 (2005).
12) J. Saltiel, D. F. Sears Jr., and A. M. Turek, *J. Phys. Chem. A* **105**, 7569 (2001).
13) T. Akitsu, M. Okawara, and K. Sano, *Asian Chem. Lett.* in press.
14) I. B. Bersuker, *Chem. Rev.* **101**, 1067 (2001).



秋津貴城
Takashiro Akitsu
東京理科大学, The University of Science
e-mail: akitsu@rs.kagu.tus.ac.jp
研究テーマ：金属錯体の構造と電子状態
趣味：読書

佐野 賢司
Kenji Sano
東京理科大学, The University of Science
研究テーマ：銅錯体の合成と構造
趣味：料理