Isotope Effects for Lattice Strain and Pseudo Jahn-Teller Distortion of Chiral Cyanide-Bridged Cu(II)-Co(III), Cr(III), and Fe(III) Bimetallic Assemblies

Takashiro Akitsu* and Satoru Sonoki

Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Abstract: By substituting H/D and 18O isotopes of water molecules, we prepared co-crystals of one-dimensional cyanide-bridged Cu(II)-Cr(III), Cu(II)-Co(III), and Cu(II)-Fe(III) bimetallic assemblies and mononuclear Cu(II) complexes, [CuL2][M(CN)6]·4H2O (L = trans-cyclohexane-(1R, 2R)-diamine; M = Cr, Co, and Fe). Solid state CD and diffuse reflectance electronic spectra exhibited typical difference of metal ions and little isotope effects. While H/D isotope effects emerged as differences of small intermolecular magnetic interactions and obvious shifts of IR bands. Though all compounds exhibited positive thermal expansion of lattice, crystal structures exhibited slight differences associated with Jahn-Teller distortion around Cu(II) coordination environment.

Keywords: Lattice distortion, Jahn-Teller effect, copper, cyanide, isotope.

INTRODUCTION

Recently, we have reported thermally-accessible lattice strain and local pseudo Jahn-Teller distortion of [CuL2][M(CN)6]·4H2O (L = trans-cyclohexane-(1R, 2R)-diamine; M = Cr, Co, and Fe) [1]. In its crystal packing of co-crystals of one-dimensional cyanide-bridged Cu(II)-Cr(III), Cu(II)-Co(III) [1], and Cu(II)-Fe(III) [2] bimetallic assemblies and mononuclear Cu(II) complexes, (pseudo) Jahn-Teller effect plays an important role in flexible distortion of crystal structures especially Cu(II)coordination environment. Theoretically, it may be expected that whether magnetic orbital of Cu(II) ion is d_{2y2} or d_{x2-y2} depends on ligand field strength and bond lengths of axial ligands [3, 4]. Additionally, configuration interaction between 3d_{x2} and 4s orbitals mixing is also subjected to tetrahedral as well as tetragonal distortion of Cu(II)coordination environment [5]. However, temperature dependence of pseudo Jahn-Teller distortion of Cu(II) moieties has not been investigated in multi-dimensional cyanide-bridged crystal lattices except for these examples [6, 7]. The results suggested that structural changes associated with pseudo Jahn-Teller distortion of mononuclear trans-[CuL2(H2O)2]2+ moiety induced by external conditions was larger than that of Cu(II) moieties in cyanide-bridged crystal lattices, ([CuL2][M(CN)6]2-)·2H2O, whose hydrogen bonds might dominate lattice strain [8-12].

Herein, we investigate isotope effects for [CuL2][M(CN)6]·4H2O (L = trans-cyclohexane-(1R, 2R)-diamine; M = Cr, Co, and Fe) about water molecules by substituting H/D and 18O isotopes (H, D, and O) (abbreviated as Cu-CrH, Cu-CrD, Cu-CrO, Cu-CoH, Cu-CoD, Cu-CoO, Cu-FeH, Cu-FeD, and Cu-FeO), which may be an important factor for the mononuclear trans-[CuL2(H2O)2]2+ moiety. Solid state CD, diffuse reflectance electronic, and IR spectra, magnetic measurements, and powder and single crystal structure analyses were carried out.

MATERIALS AND METHODOLOGY

General Procedure

Chemicals and solvents of the highest commercial grade available (Kanto Chemical, Tokyo Chemical Industry, and Wako) were used as received without further purification.

Preparations

[CuL2][M(CN)6]·4H2O, Cu-CrH, Cu-CrD, Cu-CrO, Cu-CoH, Cu-CoD, Cu-CoO, Cu-FeH, Cu-FeD, Cu-FeO, were prepared in similar way to the analogous compounds [1, 2] by employing the corresponding metal sources and water containing isotope atoms.

Preparations of Cu-CrH

Yield 88.1 %. Anal. Calcd. for C_{48}H_{82}CrCu_{3}N_{24}O_{4}: C, 42.27; H, 6.80; N, 24.64. Found: C, 42.34; H, 6.79; N, 24.62. IR (cm⁻¹, KBr): 2127 (C=N). XRD (2θ/degree, λ = 1.54184 Å) 16.94 and 16.67 for (1 -2 1), 5.77 and 5.80 for (0 0 1), 7.37 and 7.31 for (0 1 0), 8.00 and 7.92 for (0 -1 1), and 11.11 and 11.14 for (1 0 -1) at 100 and 300K, respectively.

Preparations of Cu-CrD

Yield 93.0 %. Anal. Calcd. for C_{48}H_{82}^{2-}H_{2}CrCu_{3}N_{24}O_{4}: C, 42.03; H, 6.76; N, 24.51. Found: C, 42.37; H, 6.71; N, 24.38. IR (cm⁻¹, KBr): 2127 (C≡N). XRD (2θ/degree, λ = 1.54184 Å) 17.05 and 16.82 for (1 -2 1), 5.83 and 5.77 for (0 0 1), 7.40 and 7.34 for (0 1 0), 8.06 and 7.95 for (0 -1 1), and 11.19 and 11.17 for (1 0 -1) at 100 and 300K, respectively.

*Address correspondence to this author at the Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan; Tel: +81-3-5228-8271; Fax: +81-3-5261-4631; E-mail: akitsu@rs.kagu.tus.ac.jp

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Isotope Effects for Lattice Strain and Pseudo Jahn-Teller Distortion

Preparations of Cu-CrO

Yield 88.8 %. Anal. Calcd. for C₄₈H₉₂Cr₂Cu₃N₂₄O₂: C, 42.02; H, 6.76; N, 24.50. Found: C, 42.06; H, 6.59; N, 24.50. IR (cm⁻¹, KBr): 2127 (C≡N). XRD (2θ/degree, λ = 1.54184 Å) 17.02 and 16.79 for (1 -2 1), 5.80 and 5.74 for (0 0 1), 7.40 and 7.31 for (0 1 0), 8.03 and 7.92 for (0 -1 1), and 11.22 and 11.14 for (1 0 -1) at 100 and 300K, respectively.

Preparations of Cu-CoH

Yield 76.3 %. Anal. Calcd. for C₄₈H₈₂Co₂Cu₃N₂₄O₄: C, 41.84; H, 6.73; N, 24.40. Found: C, 41.57; H, 6.58; N, 24.13. IR (cm⁻¹, KBr): 2114 (C≡N). XRD (2θ/degree, λ = 1.54184 Å) 11.43 and 11.34 for (1 0 -1), 11.80 and 11.69 for (0 0 2), 12.30 and 12.15 for (1 -1 0), 19.46 and 19.29 for (1 -2 2), and 21.58 and 21.43 for (1 -1 3) at 100 and 300K, respectively.

Preparations of Cu-CoD

Yield 78.3 %. Anal. Calcd. for C₄₈H₈₂²H₂Co₂Cu₃N₂₄O₂: C, 42.03; H, 6.76; N, 24.51. Found: C, 40.78; H, 6.74; N, 24.69. IR (cm⁻¹, KBr): 2114 (C≡N). XRD (2θ/degree, λ = 1.54184 Å) 11.37 and 11.31 for (1 0 -1), 11.75 and 11.69 for (0 0 2), 12.24 and 12.12 for (1 -1 0), 19.46 and 19.37 for (1 -2 2), and 21.55 and 21.49 for (1 -1 3) at 100 and 300K, respectively.

Preparations of Cu-CoO

Yield 74.4 %. Anal. Calcd. for C₄₈H₈₂Co₂Cu₃N₂₄O₄: C, 41.60; H, 6.69; N, 24.26. Found: C, 41.67; H, 6.70; N, 24.21. IR (cm⁻¹, KBr): 2114 (C≡N). XRD (2θ/degree, λ = 1.54184 Å) 11.37 and 11.31 for (1 0 -1), 11.72 and 11.69 for (0 0 2), 12.27 and 12.12 for (1 -1 0), 19.49 and 19.37 for (1 -2 2), and 21.55 and 21.37 for (1 -1 3) at 100 and 300K, respectively.

Preparations of Cu-FeH

Yield 73.8 %. Anal. Calcd. for C₄₈H₈₂Cu₃Fe₂N₂₄O₂: C, 42.03; H, 6.76; N, 24.51. Found: C, 41.90; H, 6.87; N, 24.28. IR (cm⁻¹, KBr): 2102 (C≡N). XRD (2θ/degree, λ = 1.54184 Å) 5.86 and 5.83 for (0 1 0), 7.40 and 7.37 for (1 0 0), 8.03 and 7.95 for (0 0 1), 11.31 and 11.28 for (1 -1 0), and 19.43 and 19.37 for (2 1 1) at 100 and 300K, respectively.

Preparations of Cu-FeD

Yield 91.9 %. Anal. Calcd. for C₄₈H₈₂²H₂Cu₃Fe₂N₂₄O₂: C, 42.03; H, 6.76; N, 24.51. Found: C, 42.37; H, 6.71; N, 24.38. IR (cm⁻¹, KBr): 2102 (C≡N). XRD (2θ/degree, λ = 1.54184 Å) 5.86 and 5.86 for (0 1 0), 7.40 and 7.37 for (1 0 0), 8.03 and 7.98 for (0 0 1), 11.34 and 11.28 for (1 -1 0), and 19.43 and 19.27 for (2 1 1) at 100 and 300K, respectively.

Preparations of Cu-FeO

Yield 89.9 %. Anal. Calcd. for C₄₈H₈₂Cu₃Fe₂N₂₄O₂: C, 41.78; H, 6.72; N, 24.36. Found: C, 41.87; H, 6.78; N, 24.40. IR (cm⁻¹, KBr): 2102 (C≡N). XRD (2θ/degree, λ = 1.54184 Å) 5.89 and 5.83 for (0 1 0), 7.40 and 7.31 for (1 0 0), 8.03 and 7.92 for (0 0 1), 11.31 and 11.14 for (1 -1 0), and 19.43 and 19.43 for (2 1 1) at 100 and 300K, respectively.

Physical Measurements

Elemental analyses (C, H, N) were carried out on a Perkin Elmer 2400II CHNS/O analyzer at Tokyo University of Science. Infrared spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer in the range of 4000-400 cm⁻¹ at 298 K. Electronic spectra were measured on a JASCO V-570 UV/VIS/NIR spectrophotometer in the range of 800-200 nm at 298 K. Circular dichroism (CD) spectra were measured on a JASCO J820 spectropolarimeter in the range of 800-200 nm at 298 K. Powder XRD patterns were also measured by using synchrotron radiation beamline at KEK-PF BL-8B with 8 keV (λ = 1.5418 Å) under variable temperature apparatus of nitrogen stream equipped with a RI-GAKU imaging plate. All the samples were measured for 3 min and constant ring current (440 mA). The magnetic properties were investigated with a Quantum Design MPMS-XL and SS superconducting quantum interference device magnetometer (SQUID) at an applied field 0.5 T in a temperature range 5-300 K. Powder samples were measured in a pharmaceutical cellulose capsule. The apparatus signals and the diamagnetic corrections were evaluated from Pascal’s constants.

X-ray Crystallography

Blue violet prismatic single crystals of Cu-CoH (0.26 x 0.20 x 0.18 mm), Cu-CoD (0.26 x 0.24 x 0.19 mm), and Cu-CoO (0.20 x 0.18 x 0.16 mm) were glued on top of a glass fiber and coated with a thin layer of epoxy resin to measure the diffraction data. The X-ray intensities were measured at 130 K for Cu-CoH and Cu-CoO and 100, 130 and 296 K for Cu-CoD with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker APEX2 CCD diffractometer. The structures were solved by direct methods using SHELXS97 [13] and expanded by Fourier techniques in a SAIN'T program package [14] (including SHELXTL version). The structures were refined on F² anisotropically for non-hydrogen atoms by full-matrix least-square methods with SHELXL97 [13]. Empirical absorption corrections were applied by a program SADABS [15]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in geometrically calculated position and refined by using riding model. Since hydrogen atoms could not be observed in the different Fourier map, we could not introduce hydrogen atoms of water molecules connected to O1 through O5 atoms. Although residual electron density was also found in the difference Fourier maps, the models containing these peaks as water molecules resulted in increase of R-values. Therefore, we could not assign them and we could not discuss hydrogen bonds closely. These bad results in refinement are mainly due to thermal vibration of oxygen atoms of crystalline water.

Crystallographic data for Cu-CoH. [T = 130(2) K] C₄₈H₈₂Co₂Cu₃N₂₄O₅, triclinic, P1, a = 8.3377(11) Å, b = 12.6477(16) Å, c = 16.018(2) Å, α = 105.755(2)°, β = 99.018(2)°, γ = 95.841(2)°, and V = 1588.6(4) Å³, and Z = 1, Dc = 1.449 Mgm⁻³, R = 0.0369, wR2 = 0.1343 (7894 reflections), S = 0.787, μ = 1.561 mm⁻¹. Flack value is equal to -0.006(18).

Crystallographic data for Cu-CoD. [T = 130(2) K] C₄₈H₈₂Co₂Cu₃N₂₄O₄, triclinic, P1, a = 8.3228(11) Å, b =
12.6426(17) Å, c = 16.007(2) Å, α = 105.579(2)°, β = 99.058 (2)°, γ = 95.799(2)°, and V = 1583.9(4) Å³, and Z = 1, D = 1.453 Mg m⁻³, R₁ = 0.0317, wR₂ = 0.0907 (9786 reflections), S = 0.825, μ = 1.566 mm⁻¹. Flack value is equal to 0.019(11).

Crystallographic data for Cu-CoD. [T = 100(2) K]
C₄₈H₈₈Co₂Cu₃N₂₄O₅, triclinic, P1, a = 8.3374(3) Å, b = 12.6329(5) Å, c = 16.0129(6) Å, α = 105.45(2)°, β = 99.11(2)°, γ = 95.7310(10)°, and V = 1587.13(10) Å³, and Z = 1, Dc = 1.454 Mg m⁻³, R₁ = 0.0241, wR₂ = 0.0667 (9322 reflections), S = 0.955, μ = 1.563 mm⁻¹. Flack value is equal to -0.012(8).

Crystallographic data for Cu-CoD. [T = 296(2) K]
C₄₈H₈₆Co₂Cu₃N₂₄O₅, triclinic, P1, a = 8.3941(4) Å, b = 12.7209(7) Å, c = 16.1119(9) Å, α = 105.7130(10)°, β = 98.6270(10)°, γ = 96.2530(10)°, and V = 1617.07(15) Å³, and Z = 1, D = 1.425 Mg m⁻³, R₁ = 0.0288, wR₂ = 0.0760 (9518 reflections), S = 1.027, μ = 1.534 mm⁻¹. Flack value is equal to -0.003(9).

RESULTS AND DISCUSSION
CD and Diffuse Reflectance Electronic Spectra

Fig. (1) shows solid state CD (as KBr pellets) and diffuse reflectance electronic spectra for Cu-Cr, Cu-Fe, and Cu-Co (H, D, and O) complexes. For Cr(III), Fe(III), and Co(III) complexes, little differences by isotope effects could be observed, while drastic differences of CT (charge transfer) bands could be observed by substituting metal ions, namely
Isotope Effects for Lattice Strain and Pseudo Jahn-Teller Distortion

The Open Crystallography Journal, 2011, Volume 4

11

[Cr(CN)₆]³⁻, [Fe(CN)₆]³⁻, and [Co(CN)₆]³⁻. Previously, we also reported that CD spectra as follows [1]: a positive peak at 19300 cm⁻¹ and negative peaks at 16600 cm⁻¹ and 34000 cm⁻¹ for Cu-CrH, a positive peak at 19100 cm⁻¹, 27000 cm⁻¹ (shoulder), and a negative peak at 31600 cm⁻¹ for Cu-CoH, and positive d-d peak at 14500 cm⁻¹, positive CT peak at 18900 cm⁻¹, and negative CT peak at 28600 cm⁻¹ for Cu-FeH [2]. The corresponding diffuse reflectance electronic spectra were reported as follows [1, 2, 16]: d-d bands appeared at 19100, 19800, and 19400 cm⁻¹, π-π* bands appeared at 28900, 26000, and 26500 cm⁻¹ for Cu-CrH, Cu-CoH, and Cu-FeH, respectively, and CT bands appeared at 600 and 22900 cm⁻¹ for Cu-CoH and Cu-FeH, respectively.

**Magnetic Properties**

Fig. (2) shows temperature dependence of the \( \chi_m T \) values per [CuL₂][M(CN)₆]·4H₂O units of a powder sample of Cu-Cr, Cu-Co, and Cu-Fe (H, D, and O) complexes at 0.5 T. All three compounds are composed of paramagnetic onedimensional Cu²⁺M³⁺ chains and paramagnetic mononuclear Cu²⁺ moiety, though superexchange interactions through cyanide-bridged are mainly dependent on [Cr(CN)₆]³⁻, [Fe(CN)₆]³⁻, and [Co(CN)₆]³⁻ moieties regardless of isotopes effects. For example, we have reported for Cu-CoH in the previous paper [1] as follows: The \( \chi_m T \) value is 0.694 cm³Kmol⁻¹ at 300 K, which is smaller than the expected value (1.625 cm³Kmol⁻¹) for uncoupled Cu²⁺Co³⁺ system of

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Fig. (1). [above] Solid State CD (as KBr pellets) and [below] diffuse reflectance electronic spectra for [left] Cu-Cr (H [blue], D [red], and O [green]), [middle] Cu-Fe (H, D, and O), and [right] Cu-Co (H, D, and O) complexes at 300 K.
Co$^{III}$ (S = 0) and Cu$^{II}$ (S = 1/2). On cooling, the $\chi''T$ value gradually increases up to 1.10 cm$^3$/mol at 5 K. However, slight isotope effects (H, D, and O) within the same compounds must be ascribed to intermolecular hydrogen bonds.

**IR spectra**

Fig. (3) shows IR spectra of Cu-Cr, Cu-Co, and Cu-Fe (H, D, and O) complexes. The features of cyanide stretching bands depend on the types (bridged or terminal) of cyanide ligands and weight of metal ions (namely [Cr(CN)$_6$]$^{3-}$, [Fe(CN)$_6$]$^{3-}$, and [Co(CN)$_6$]$^{3-}$ moieties), and appear at 2127, 2114, and 2102 cm$^{-1}$, respectively. However, little isotope effects could be observed as cyanide stretching bands for all three compounds (see preparations). The splitting of cyanide bands is attributed to the types of cyanide ligands, which is not clear (not shown) [1]. Although O-H bands can vary by both D and $^{18}$O substitution, characteristic band shift around 830, 880, 1200 cm$^{-1}$ could be observed only for Cu-CrD, Cu-CoD, and Cu-FeD obviously. The H/D isotope effects emerged as differences of small intermolecular magnetic interactions and clear shift of IR bands.

**Crystal Structures**

Fig. (4) shows important parts of crystal packing of Cu-CoD, which is isostructural to previously reported Cu-Co, Cu-Cr, and Cu-Fe essentially. Tables 1 and 2 summarize selected (axial elongated bonds due to Jahn-Teller distortion of three Cu(II) atoms) isotope differences of Cu-Co (H, D, and O) complexes at 130 K and temperature dependence of Cu-CoD at 100, 130, and 296 K respectively. As mentioned for the IR spectra of isotope effects caused by H/D or $^{16}$O/$^{18}$O substitution, structural differences caused by hydro-
Isotope Effects for Lattice Strain and Pseudo Jahn-Teller Distortion

The Open Crystallography Journal, 2011, Volume 4

gen bonds or atomic weight of water molecules may be ex-
pected for crystal structures. However, structural evidence of
isotopes of water molecules could not be detected as Jahn-
Teller distorted Cu(II) coordination environment not other
positions of non-hydrogen atoms for Cu-Co (H, D, and O)
complexes. Previously, we reported that thermally crystal
changes associated with pseudo Jahn-Teller effect for Cu-Co
and Cu-Cr could be significantly found in axial bond dis-
tances of the mononuclear trans-[CuL₂(H₂O)₂]²⁺ moiety,
while not found in Cu(II) moieties involved cyanide-bridged
crystal lattices, [[CuL₂]₂[M(CN)₆]₂]²⁻2H₂O [1]. As stated in
the preparations section, powder XRD by means of synchro-
tron radiation exhibited positive thermal expansion of crystal
lattice for all compounds of Cu-Co, Cu-Cr, and Cu-Fe
(H, D, and O) complexes at 100 and 300 K normally. They
exhibit positive thermal expansion as a function of tempera-
ture continuously without structural phase transition, and do
not exhibit negative thermal expansion of cyanide complexes
[17-20] accompanying with losing crystalline water mole-
cules. In general, O-D hydrogen bonds are weaker than O-H
ones. Although little structural differences between Cu-CrH
and Cu-CrD could be observed at constant temperature of
130 K, temperature dependences of local geometries for
Cu-CrD are investigated at 100 and 298 K. However, Table
indicated normal structural changes even for Cu-CoD. In
this way, differences detected by IR spectra and magnetic
properties among H, D, and O complexes are too slight to
detect crystallographically [21] in the range of our study by
present procedures.

Fig. (3). IR spectra for for [above] Cu-Cr (H [plain], D [gray], and O [bold]), [middle] Cu-Fe (H, D, and O), and [below] Cu-Co (H, D, and O) at 300 K.
CONCLUSION

By substituting H/D and $^{18}$O isotopes of water molecules, we prepared bimetallic assemblies, Cu-CrH, Cu-CrD, Cu-CoH, Cu-CoD, Cu-CoO, Cu-CoH, Cu-CoD, Cu-CoO, Cu-FeH, Cu-FeD, and Cu-FeO. Solid state CD and diffuse reflectance electronic spectra exhibited typical difference of d-d and CT bands due
to Cr(III), Co(III), and Fe(III) metal ions without obvious differences due to isotopic effect. Tuning of strength of intermolecular hydrogen bonds by substituting H/D better than 16O/18O resulted in small differences of magnetic properties and significant shift of IR bands associated with O-D bands. However, structural evidence of isotopes of water molecules could not be detected as Jahn-Teller distorted Cu(II) coordination environment nor displacement of non-hydrogen atoms. Additionally, powder XRD by means of synchrotron radiation exhibited normally positive thermal expansion of crystal lattice for all compounds.

SUPPLEMENTARY DATA

CCDC (782124-782418) contains the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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