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Synthesis and crystal structures of the flexible Schiff base complex bis(*N*-1,2-diphenylethyl-salicydenaminato-κ^2N,O)copper(II) (methanol): A rare case of solvent-induced distortion

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Abstract

A new mononuclear copper(II) complex incorporating a bulky Schiff base ligand, bis(*N*-1,2-diphenylethyl-salicydenaminato-κ^2N,O)copper(II) (green form) and its co-crystal containing methanol solvent molecules (brown form) have been synthesized and characterized by X-ray crystallography, XRD, IR and diffuse reflectance spectra in the solid state. This is a rare case in that both solvent free and containing crystals can be isolated and characterized. Both forms adopt a compressed tetrahedral *trans*-[CuN_2O_2] coordination geometry with coordination bond angles of *trans*-N–Cu–N = 157.0(4)° and *trans*-O–Cu–O = 151.1(3)° for the brown form and *trans*-N–Cu–N = 141.3(3)° and *trans*-O–Cu–O = 139.9(2)° for the green form. The methanol solvent molecules force the complex of the brown form to adopt a more planar coordination environment in the solid state. Semi-empirical calculations (ZINDO) revealed the magnitude of the dipole moment of both molecules and that the energy of the green form is 5.7 kJ mol^{-1} higher than that of the brown form. In addition, absorption spectra in various organic solvents were measured and a relationship between absorption spectra and polarity of the solvents is discussed.

Keywords: Copper(II) complexes; Crystal structures; Schiff base; Solvent

1. Introduction

In recent years, functional materials of transition metal complexes whose physical properties can be controlled by various external perturbations, such as light irradiation, have been attracting great interest [1,2]. A general strategy to achieve such photo-switching materials has not been established as yet. One of the hypotheses may be examining candidates which exhibit structural isomerism or structural phase transitions, induced by other external conditions, with a small energy barrier, for example, temperature, pressure, solvents and so on. Thus, thermochromic [3–5], piezochromic [6,7], solvatochromic [8–10] and vapochromic [11,12] complexes may be suitable for this purpose. It has been well known that a series of bis(*N*-alkyl-salicylideneimine)copper(II) complexes incorporating Schiff base ligands [13] exhibit flexible structural changes of coordination spheres from square planar to tetrahedral depending on steric and/or electronic effects of the ligands, such as bulky substituents [14–17] and chirality [18–22]. Furthermore, they also exhibit structural isomers [23], thermally induced structural phase transitions [24–28] and solvatochromism [13]. Indeed, some other copper(II) complexes incorporating monodentate amine ligands easily vary their coordination geometries depending on systematic steric effects of ligands such as 1,2-diphenylethylamine [29] and chirality, for example of 1-phenylethylamine [30,31] or 1-cyclohexylethylamine [30]. However, so far it has been rare that structural distortion is induced by guest molecules into host mononuclear copper(II) complexes [32,33]. We report here a structural comparison of the bis(*N*-1,2-diphenylethyl-salicydenaminato-κ^2N,O)copper(II) complex (green form) and its co-crystal containing metha-

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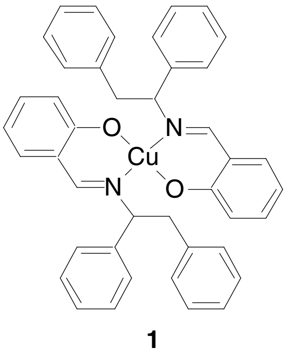

2 = **1** • CH_3OH

Scheme 1.

nol solvent molecules (brown form). Guest methanol molecules force the complex to adopt a more planar coordination environment in the solid state. In addition, absorption spectra in various organic solvents have been measured and a relationship is found between the features of absorption spectra and polarity of solvents as chemical external perturbations (Scheme 1).

2. Experimental

2.1. General

Chemicals of the highest commercial grade available (Aldrich and Wako) were used as received without further purification. Elemental analyses (C, H, N) were carried out on an Elementar Vario EL analyser at Keio University. Infrared spectra were recorded as KBr pellets on a JASCO FT-IR 660 plus spectrophotometer in the range of 4000–400 cm^{-1} at 298 K. Thermal analysis was performed on a SHIMADZU DSC-60 differential scanning calorimeter (DSC), where the heating rate was 10 K min^{-1} in the range 313–673 K. Diffuse reflectance spectra were measured on a JASCO V-560 spectrophotometer equipped with an integrating sphere in the range 850–220 nm at 298 K. Absorption spectra were measured on a JASCO V-560 spectrophotometer in the range 900–200 nm at 298 K. Magnetic susceptibility was measured with a Sherwood Scientific magnetic susceptibility balance at 298 K. Magnetic data were corrected for the magnetization of diamagnetic contributions, which were estimated from Pascal constants. XRD were recorded on a Rigaku RAD-C diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Semi-empirical molecular orbital calculations were performed the program ZINDO in a CAChe software package based on the crystal structures determined.

2.2. Synthesis

Treatment of an equimolar amount of copper(II) acetate (0.91 g, 5.00 mmol), salicylaldehyde (1.22 g, 10.0 mmol) and 1,2-diphenylethylamine (1.97 g, 10.0 mmol) in ethanol (100 mL) at 318 K for 3 h gave rise to brown crude precipitates. Recrystallization from an acetone solution at 298 K over a period of several days yielded green plate-like crystals suitable for X-ray crystallography, green form (**1**). *Anal.* Calc. for $C_{42}H_{36}CuN_2O_2$: C, 75.94; H, 5.46; N, 4.22. Found: C, 75.68; H, 5.37; N, 4.17%. IR (KBr): 1610 cm^{-1} (imine C=N stretching band). M.p. 572 K (decomposition). $\mu_{eff} = 1.52$ BM at 298 K. On the other hand, recrystallization from methanol–acetone mixed solution (1:1, v/v) at 298 K over a period of several days yielded a brown precipitate. *Anal.* Calc. for $C_{42}H_{36}CuN_2O_2$: C, 75.94; H, 5.46; N, 4.22. Found: C, 75.84; H, 5.46; N, 4.12%. IR (KBr): 1609 cm^{-1} (imine C=N stretching band). M.p. 559 K (decomposition). $\mu_{eff} = 1.43$ BM at 298 K. Well-grown brown prismatic single crystals suitable for X-ray crystallography contain methanol molecules, brown form (**2**).

2.3. X-ray crystallography

Intensity data were collected on a Rigaku AFC-7R four-circle diffractometer. The structures were solved by direct methods using SIR92 [34] and expanded by Fourier techniques. The structures were refined on F^2 anisotropically for non-hydrogen atoms by full-matrix least-squares methods with SHLEXL-97 [35] of the teXsan program package [36]. Empirical absorption corrections were applied based on ψ scans; transmission factors for **1** and **2** were 0.726–0.933 and 0.919–0.999, respectively. No significant decay in the intensity of three standard reflections was observed throughout the data collection. The hydrogen atoms were located at geometrically calculated positions, C–H = 0.950 Å, and refined isotropically. All the non-hydrogen atoms were refined anisotropically. As for **2**, C8(H6A)–C9A(H7A, H8A) and C8(H6B)–C9B(H7B, H8B) were treated as a positional disorder with 0.5 occupancy. Crystallographic data for **1** and **2** are summarized in Table 1.

3. Results and discussion

3.1. Description of structures

The molecular and crystal structures of **1** and **2** are depicted in Figs. 1–4, respectively. Selected bond distances and angles, and torsion angles of **1** and **2** are given in Tables 2 and 3, respectively.

The green form (**1**) affords a compressed tetrahedral *trans*-$[CuN_2O_2]$ coordination geometry, in which the bidentate chelate ligands coordinate to the copper ion through phenolate oxygen atoms and imine nitrogen atoms. The Cu–N bond distances are 1.959(10) and 1.990(9) Å, while the Cu–O bond distances are 1.877(7) and 1.885(8) Å. These values are comparable to related non-planar or distorted tetrahedral complexes [16,17,19,22]. The *trans*-N–Cu–N and *trans*-O–Cu–O bond angles are 157.0(4)° and 151.1(3)°, respectively. The dihedral angle between the O1/Cu1/N1 plane and the O2/Cu1/N2 plane is 36.46(1)°,