



Copper(II) solvatochromic complexes [Cu(acac)(*N*^{*N*})(ligand)]BPh₄ with various axial ligands. Correlation between coordination geometries and d–d transition energies (acac = acetylacetonato, *N*^{*N*} = 1,10-phenanthroline, 2,2'-bipyridyl)

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ABSTRACT

A series of copper(II) solvatochromic complexes [Cu(acac)(*N*^{*N*})(ligand)]BPh₄ (acac = acetylacetonato; *N*^{*N*} = 1,10-phenanthroline (**1**), 2,2'-bipyridyl (**2**); ligand = HMPA, pyridine, DMSO, DMF, MeOH, acetone, and MeCN) have been synthesized and their coordination geometries were crystallographically investigated. The solvent-coordinated cations, adopting a five-coordinate square-pyramidal structure, formed head-to-tail dimers via $\pi \cdots \pi$ interactions. Solid-state absorption studies revealed that their d–d transition energies are correlated with the donor number of the axial ligands. A linear correlation was found between the d–d transition energies and the Cu–O (axial ligands) distances in the solid-state, revealing the role of the coordination environment on the d–d transition energies in the copper(II) solvatochromic complexes.

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1. Introduction

Chromotropism of coordination compounds, or color change due to external stimuli, is an interesting phenomenon and is generally ascribed to transformation of coordination geometry around the metal center [1–5]. In particular, the solvatochromism of metal complexes have attracted special attention because of their potential application for color indicators and optical sensors [1–3,6]. To date, many copper(II) solvatochromic complexes with mixed ligands have been reported, in which chelate ligands of β -diketonato and ethylenediamine derivatives are often used [1–16]. Solutions of these complexes show color changes from green via blue to violet, depending on the solvent. The color change originates from the shift of the d–d absorption bands of the copper(II) center by coordination of the solvent molecules. The absorption energies are known to correlate with the donor number (DN) of the coordinated solvents [1–16]. In the solvent-coordinated species, the coordination geometries around the metal center should be a crucial factor that determines the d–d absorption energies. However, a systematic study of the correlation between the coordination environments and the d–d absorption bands of metal(II) solvatochromic complexes has not been reported, whereas there have been a few

structural reports on solvent coordinated copper(II) solvatochromic complexes [8,12].

In this context, to investigate solvent dependence of the coordination environment and its consequence on the solvatochromism, we have designed square planar complexes [Cu(acac)(*N*^{*N*})]BPh₄ {acac = acetylacetonato, *N*^{*N*} = 1,10-phenanthroline (phen) (**1**) or 2,2'-bipyridyl (bpy) (**2**)} (Fig. 1), expecting that the use of planar ligands leads to $\pi \cdots \pi$ interactions and which consequently provides crystalline materials suitable for crystallography. In fact, copper(II) complexes with β -diketonato and aromatic *N*-donor ligands have been used as building blocks for supramolecular architectures [17–21]. Most of such complexes are anion-coordinated neutral species, and have not been investigated from chromotropic aspects. We expected that the use of a bulky and non-coordinating counter anion, BPh₄[−], provides space for solvent coordination to the metal centre in the crystalline state, which enables direct comparison of the chromic properties in solution and in the solid state. Here we report the preparation, crystal structures, and absorption spectra of unsolvated **1**, **2**, and their solvated states with a wide range of DN, from HMPA (168 kJ mol^{−1}) to MeCN (59 kJ mol^{−1}). A correlation was found between the coordination environments, solid state d–d transition energies, and DN of the axial ligands (i.e. solvent). To our knowledge, this is the first study elucidating the structure–property relationship of solvatochromic copper(II) complexes.

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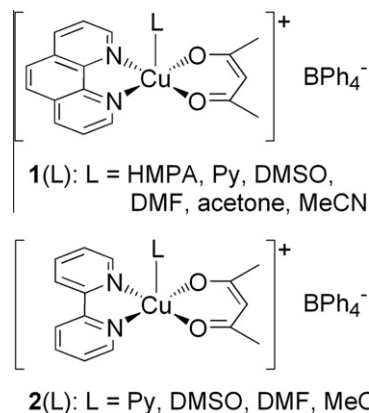


Fig. 1. Illustrations of **1**, **2** and their solvated derivatives.

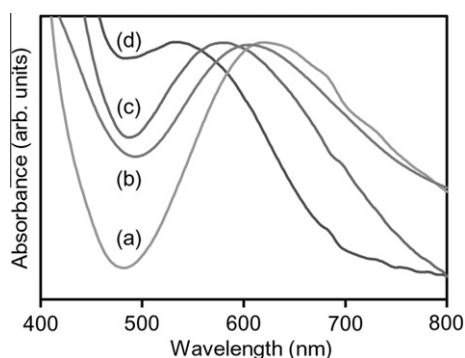


Fig. 2. Solid state UV-Vis absorption spectra of **1** and its solvent coordinated derivatives: (a) **1**(HMPA), (b) **1**(DMSO), (c) **1**(acetone) and (d) **1**.

Table 1
d-d Transition energies (ν_{\max}) in **1**, **2**, and their solvated complexes in the solid state.

Axial ligand	Compound	ν_{\max} (cm ⁻¹)	Compound	ν_{\max} (cm ⁻¹)	Donor number [37] (kJmol ⁻¹)
HMPA	1 (HMPA)	15 456			162
Py	1 (Py)	16 667	2 (Py)	16 502	138
DMSO	1 (DMSO)	16 129	2 (DMSO)	16 474	125
DMF	1 (DMF)	16 447	2 (DMF)·DMF	16 611	111
MeOH			2 (MeOH)	17 182	79
Acetone	1 (acetone)	17 212			71
MeCN	1 (MeCN)·MeCN	17 094			59
None	1	18 762	2	19 084	0

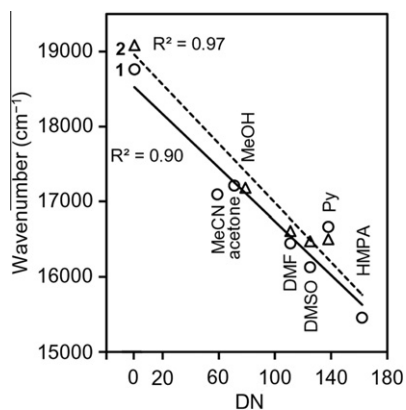


Fig. 3. Solid state d-d transition energies of the solvated complexes derived from **1** (circles) and **2** (triangles) plotted vs. the donor number of the axial ligand. The solid line and dashed line represent linear correlations for **1** and **2**, respectively.

2. Results and discussion

2.1. Synthesis

1 and **2** were prepared by the reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with *N*-chelate ligands (*N*²) and acac in the presence of a base in EtOH, followed by anion exchange using NaBPh_4 . Recrystallization of **1** and **2** from polar solvent with relatively high donor number (DN) provided green or blue crystals of solvent-coordinated complexes, **1**(HMPA), **1**(Py), **1**(DMSO), **1**(DMF), **1**(acetone), **1**(MeCN)·MeCN,

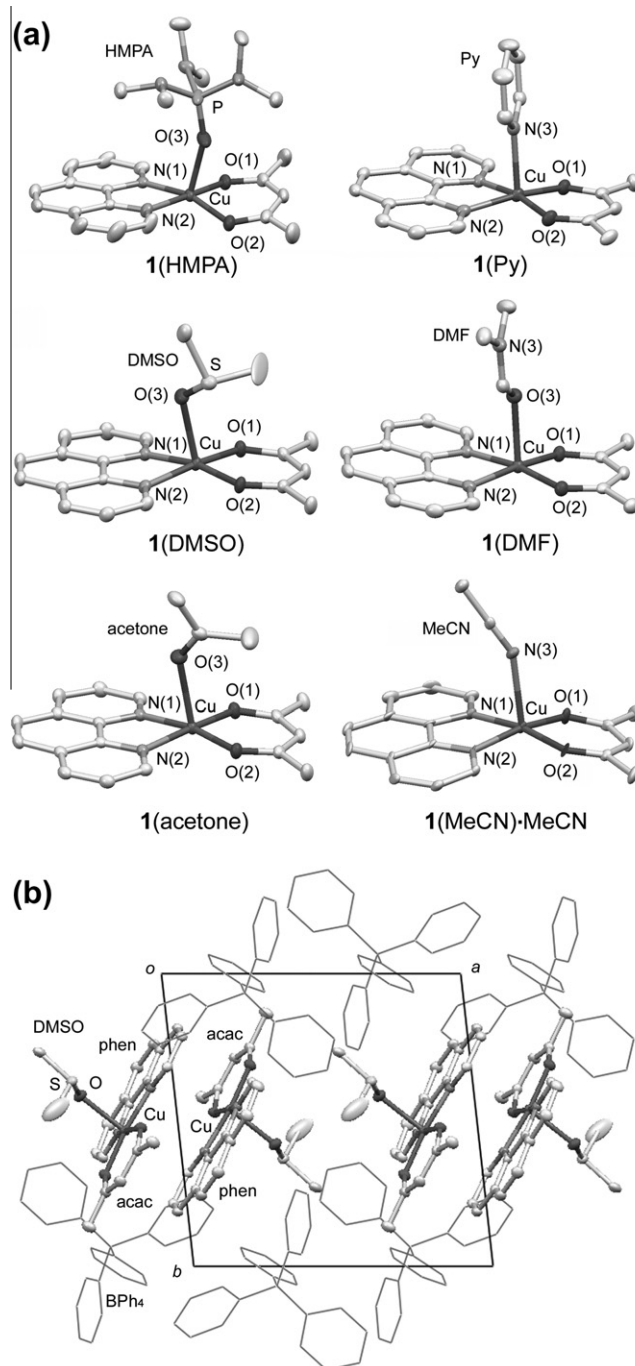


Fig. 4. (a) Molecular structures of the cations in **1**(HMPA), **1**(Py), **1**(DMSO), **1**(DMF), **1**(acetone), and **1**(MeCN)·MeCN. (b) Packing diagram of **1**(DMSO) viewed along the *c* axis, showing head-to-tail dimers of the cations. Hydrogen atoms are omitted for clarity. Only one of the disordered components of DMSO is shown for **1**(DMSO).

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