Study on imidazolate-bridged divalent copper ion complexes capped with tris(1-pyrazolyl)methane

Tamizo Kogane *, Akihiro Ondo, Masaru Yamasaki, Takuya Kanetomo, Takayuki Ishida *

Department of Engineering Science, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan

A B S T R A C T

Four kinds of non-substituted imidazolate(im)-bridged copper(II) complexes using tris(1-pyrazolyl) methane (pz$_3$CH) as a capping ligand, namely, [Cu(μ-im)(pz$_3$CH)]$_n$X$_n$ (X = BF$_4$ (**1**), ClO$_4$ (**2**), CF$_3$SO$_3$ (**3**), (SO$_4$)$_{0.5}$ (**4**)) were prepared. Their crystal structures have been determined, and despite the different space groups (orthorhombic *Pna*2$_1$ for **1**–**3** and monoclinic *P*2$_1$/*n* for **4**) and the variety of counter anions, they consist of equally-spacing polymeric chains. The Cu ion in **1**–**3** has a quasi-six-coordination environment, while the Cu ion in **4** has a nearly five-coordination one. The Bonner-Fisher model gave the exchange coupling parameters 2J/k_B = −98.2(16), −106.6(10), −102.0(6), and −104.2(8) K for **1**–**4**, respectively. The strong exchange couplings originate in the equatorial coordination of the N$_{im}$ atoms. We revealed that the magnitude of J values is influenced by the counter anion. The usability of the neutral pz$_3$CH capping ligand as well as anionic pz$_3$BH$^-$ has been shown.

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1. Introduction

For development of metal–organic frameworks based on polymeric coordination chains, supramolecular complexes, and macrocycles [1], a non-substituted imidazole anion (im) attracts much attention as a building block [2]. We have focused on the im-bridged copper(II) complexes, exploring the diversity of structures and magnetic interactions, and synthesized one-dimensional chain compounds [Cu(μ-im)(L)]$_n$ (L = nonane-4,6-dionate (dnbm$^-$) [3], 2,6-dimethylheptane-3,5-dionate (dibm$^-$) [3], hydrotris(1-pyrazolyl)borate (pz$_3$BH$^-$) [4]). A tridentate tripodal pz$_3$BH$^-$ has sometimes been chosen as a capping ligand. The im-bridged tetranuclear metallacycles such as [Cu(μ-im)(tacn)]$_4$(ClO$_4$)$_4$·2H$_2$O (tacn = 1,4,7-triazacyclononane) [2b] and [Cu(μ-im)(L)]$_4$ (L = dnbm$^-$ [3], 1-phenylbutane-1,3-dionate [3], pz$_3$BH$^-$ [4]) are also known. The charge of the capping ligands and counter anions may influence the crystal structure and accordingly magnetic coupling. Tris(1-pyrazolyl)methane (pz$_3$CH) is noted as a neutral isoelectronic analogue compared with the anionic pz$_3$BH$^-$. Its coordination compounds have been studied [5], but such examples are not so many as those of pz$_3$BH$^-$. Mononuclear iron(II) complexes with pz$_3$CH have been reported to display spin-crossover phenomenon [6].

In the present study, we employed neutral pz$_3$CH as a tripodal cap, in place of anionic pz$_3$BH$^-$, in the study of copper(II) chain complexes. We succeeded in preparation of four kinds of im-bridged copper(II) complexes [Cu(μ-im)(pz$_3$CH)]$_n$X$_n$ (X = BF$_4$ (**1**), ClO$_4$ (**2**), CF$_3$SO$_3$ (**3**), (SO$_4$)$_{0.5}$ (**4**)). We will describe the preparation, crystal structures, and the relations between the structure and magnetic property.

2. Results and discussion

2.1. Synthesis and IR spectral characterization

Four non-substituted im-bridged copper(II) complexes **1**–**4** were synthesized according to the following procedures. Compound **1** was obtained by the reaction of one molar equivalent of Cu(BF$_4$)$_2$·6H$_2$O, Him, and pz$_3$CH in the presence of triethylamine (TEA) in a water-methanol mixed solvent. Compounds **2** and **3** were prepared by a method similar to that described for **1**. Compound **4** was given by the reaction of a half molar CuSO$_4$·5H$_2$O and pz$_3$CH, and one molar Him in a water-methanol solution containing TEA (Section 4.2). We attempted to prepare possible [2 × 2] grids such as [Cu(μ-im)(pz$_3$BH)]$_4$ [4]. Unfortunately, formation of [Cu(μ-im)(pz$_3$CH)]$_4^{4+}$ framework was unsuccessful using a methanol solution with TEA or a water–methanol solution without TEA. A byproduct was characterized as a mononuclear copper(II) complex such as [Cu(pz$_3$CH)$_2$](CF$_3$SO$_3$)$_2$.

Attempted synthesis using other 3d metal ions is stated briefly. A ternary system of Ni^{2+}/Him/pz_3CH afforded two mononuclear complexes, namely $[Ni(pz_3CH)_2]X_2$ (X = BF_4 and ClO_4; as preliminarily characterized by means of crystallographic analysis),) instead of im-bridged polynuclear chains under the conditions described above. Similar monomeric complexes of Fe^{2+} [6] and Cu^{2+} [5d] are reported. On the other hand, in the Cu^{2+} case, the skeleton of polymeric chains always appeared in a water–methanol solution of a mixture of Him, Cu^{2+}, and pz_3CH with an appropriate molar ratio in the presence of TEA.

The IR spectroscopic study is compatible with the present molecular and crystal structures in **1–3**. In the spectrum of **4,** in addition to the absorption bands due to the pz_3CH ligand, two broad O–H stretching bands (v(O–H)) were found around 3390 and 3300 cm^{-1}. The v(O–H) bands shifted to a lower frequency are assigned to O–H⋯O hydrogen bonds arising from O–H group (s). This finding indicates that methanol and/or water molecules are present in **4**. Finally, the crystal structures of **1–4** were determined by means of X-ray diffraction studies (Section 4.2). The formula of a freshly prepared single crystal of **4** was determined as a solvated form $[Cu(\mu\text{-im})(pz_3CH)](SO_4)_{0.5}\cdot$solv. The elemental analysis of **4** suggests solv. = $(CH_3OH)_{0.5}\cdot(H_2O)_{1.5}$ upon storage at room temperature, while the X-ray crystallographic analysis supports solv. = $CH_3OH\cdot(H_2O)_2$ after the residual electron densities in a Fourier map were assigned to methanol. The sample of elemental analysis was analyzed after collected on a filter, washed, and dried, and solv. = $(CH_3OH)_{0.5}\cdot(H_2O)_{1.5}$ was characterized by loss of $(CH_3OH)_{0.5}\cdot(H_2O)_{0.5}$.

2.2. Crystallographic analysis

The crystal structures of **1–4** have been determined by the X-ray diffraction study. Selected crystallographic data are listed in Table 1. Despite the different space groups (orthorhombic $Pna2_1$ for **1–3** and monoclinic $P2_1/n$ for **4**) and the variety of counter anions, they exhibit a sturdy skeleton of polymeric chains. Compared with the well-studied pz_3BH^- analogues [4,5], the present compounds should have one molar monoanionic counter ion or a half molar dianionic counter ion, from the charge balance. The phase purity was confirmed with the powder X-ray diffraction study (Fig. S1, Supporting Information).

Fig. 1a shows the molecular structure of **1**. A linear chain structure is formed in a space group $Pna2_1$, which contains a $Cu(\mu\text{-im})$ repeating motif as a crystallographically independent unit. Thus, compound **1** constructs an equally-spacing chain. Compounds **2** and **3** basically possess crystal structures isomorphic of that of **1**.

It should be noted that a relatively large $CF_3SO_3^-$ ion can be accommodated in this type of crystal. As Fig 1b displays, **4** gave the practically the same skeleton of the polymeric chain regardless of the presence of SO_4^{2-} as a relatively large counter anion [7]. One Cu (μ-im) unit in **4** is crystallographically independent.

The Cu1 atom in **1–4** has a CuN_5 coordination environment. Four equatorial Cu–N distances in **1–4** are similar to those of [Cu$(\mu\text{-im})(pz_3BH)]_n$ (Table 2). While axial Cu–N distances (2.370(4)–2.457(4) Å) are rather longer than that of $[Cu(\mu\text{-im})(pz_3BH)]_n$ (2.298(6) Å). Especially, the Cu1-N7 distance in **3** is the longest (2.457(4) Å). Note that all the im nitrogen atoms occupy the equatorial sites, and we can expect considerably large exchange coupling across the im bridges.

An angular structural index parameter τ [8] can be conveniently used to distinguish between the square-pyramidal (SqP) and trigonal–bipyramidal structures. An ideal SqP structure is characterized with $\tau = 0$. The τ values were evaluated using the N1-Cu1-N3 and N2*-Cu1-N5 angles (Table 2). The τ values for Cu1 in **1–4** are 0.02, 0.007, 0.09, and 0.04, respectively, being close to zero. These values fall into the category of an SqP structure. On the other hand, the value for Cu ion for $[Cu(\mu\text{-im})(pz_3BH)]_n$ is 0.105 [4]. This means that the coordination geometry of Cu ion belongs to a slightly distorted SqP type.

The Cu1-O1 bond length is 2.511(3) Å in **3**. The O1 atom seems to be situated in the sixth position, though this distance is on a borderline between a coordination bond and weak intermolecular interaction. This means that Cu1 in **3** has a quasi-six-coordination environment. Similarly, the geometry about Cu1 in **1** and **2** appears to be a quasi-six-coordination environment (Table 2).

On the other hand, The O5 atom coming from methanol molecule seems to be situated in the sixth position. The Cu1-O5 distance of 3.173(15) Å in **4** is appreciably longer than the corresponding Cu1-O1 one in **3**. Further, the shortest Cu1-O distance related with SO_4^{2-} ion is 4.63(1) Å. This suggests that the geometry about the Cu1 ion is classified as a nearly SqP type supported by the τ value. The N1-Cu1-N3 and N2*-Cu1-N5 angles in **4** are slightly smaller than 180° (Table 2), while the corresponding angles of $[Cu(\mu\text{-im})(pz_3BH)]_n$ having a slightly distorted SqP structure are considerably small values of 165.8(3) and 172.1(2)° [4].

The Cu⋯Cu interatomic distances in **1–4** are rather shorter than that of $[Cu(\mu\text{-im})(pz_3BH)]_n$, and are similar to or slightly shorter than those of $[Cu(\mu\text{-im})(L)]_n$ (L = dnbm, dibm) (Table 3). In particular, the Cu⋯Cu interatomic one in **4** is the shortest (5.816(1) Å). This result is owing to the short imidazolate-bridged Cu1-N1 and Cu1-N2* distances (Table 2). However, the corresponding distances in $[Cu(\mu\text{-im})(pz_3BH)]_n$ are 1.986(6) and 1.993(6) Å, respectively,

Table 1
Selected crystallographic data for **1–4**.

Complex	1	2	3	4
Formula	$C_{13}H_{13}CuBF_4N_8$	$C_{13}H_{13}CuClN_8O_4$	$C_{14}H_{13}CuF_3N_8O_3S$	$C_{28}H_{42}Cu_2N_{16}O_{10}S$
Formula weight	431.65	444.30	493.91	921.89
Habit	blue platelet	blue block	green block	blue prism
Dimension (mm^3)	0.48 × 0.10 × 0.80	0.37 × 0.30 × 0.10	0.12 × 0.10 × 0.08	0.8 × 0.5 × 0.4
T (K)	100	100	100	100
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
Space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	$P2_1/n$
a (Å)	17.355(3)	17.6702(8)	18.499(5)	10.4818(9)
b (Å)	13.081(2)	13.2921(6)	12.994(3)	7.5978(12)
c (Å)	7.7039(10)	7.7653(3)	7.7682(15)	22.404(3)
β (°)	90	90	90	96.948(2)
V ($Å^3$)	1748.9(5)	1823.87(14)	1867.4(7)	1771.1(4)
Z	4	4	4	2
$R(F)^a$ ($I > 2\sigma(I)$)	0.0555	0.0587	0.0460	0.0733
$R_w(F^2)^b$ (all data)	0.1546	0.0990	0.0493	0.1012

^a $R = \Sigma\ ||F_o| - |F_c||/\Sigma|F_o|$ (unit weights).

^b $R_w = [\Sigma\ w(F_o^2 - F_c^2)^2/\Sigma\ w(F_o^2)^2]^{1/2}$.