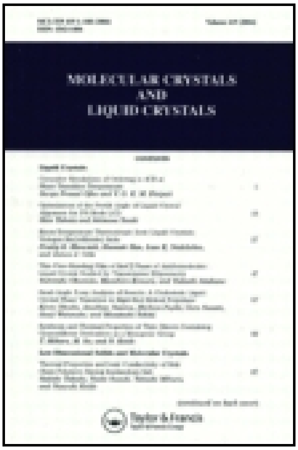

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Varieties of Crystalline Architecture by Using Hydrogen Bonding in Biimidazolate Metal Complex Systems. Part 1: Dimer Complex

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VARIETIES OF CRYSTALLINE ARCHITECTURE BY USING HYDROGEN BONDING IN BIIMIDAZOLATE METAL COMPLEX SYSTEMS.
PART 1: DIMER COMPLEX

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Abstract Two crystal structures of [Cu(tacn)(Hbim)](ClO$_4$)•MeOH (**2**) (tacn = 1,4,7-triazacyclononane) and [Cu(SalenNMe$_2$)(Hbim)]$_2$ (**1**) (salenNMe$_2$ = N-salicylidene-N',N'-dimethylethylenediamine) have been determined. The structures are the first examples of a mononuclear complex containing monodeprotonated 2,2'-biimidazolate (Hbim$^-$) as a bidentate ligand.

INTRODUCTION

Molecular systems with cooperative interaction between hydrogen bonding (HB) and charge-transfer (CT), the HBCT systems, can be a good candidate for new molecular materials having interesting solid state properties.[1,2]

Such an idea can be examined and developed by expanding the HBCT systems into the transition metal systems having both hydrogen bonding and CT type interactions.[3-5] As the first step, we have intended to construct the hydrogen bonded transition metal complexes having a direct intermolecular hydrogen bonding.

Selecting the 2, 2'-biimidazole ligand (H$_2$bim), the monomeric complex containing the triazamacrocycle ligand, 1,4,7-triazacyclononane (tacn) and the bidentate mono-deprotonated 2,2'-biimidazolate ligand (Hbim$^-$), [Cu(tacn)(Hbim)]ClO$_4$ (**1**) is synthesized and characterized by X-ray crystal structure analysis. The complex of [Cu(salenNMe$_2$)(Hbim)]$_2$ (**2**) containing tridentate ligand of N-salicylidene-N',N'-dimethyl-ethylenediamine (salenNMe$_2$) and the Hbim$^-$ ligand is also synthesized and characterized by X-ray crystal structure analysis, which is the first example of the dimeric hydrogen bonded transition metal systems (Figure 1).

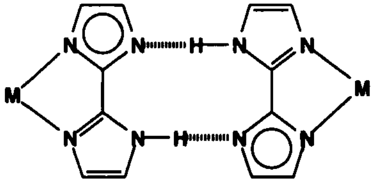

FIGURE 1 Hydrogen bonding dimer by metal complexes with Hbim⁻ ligands.

EXPERIMENTAL

Measurement

Intensity data were collected at a temperature of 296 K on a Rigaku AFC5R diffract meter with graphite-monochronated Mo-Kα radiation and the ω–2θ scan technique. Accurate cell dimensions and crystal orientation matrixes were determined by least-squares refinement of 25 reflections for compounds **1** and **2**. The crystallographic data and structure refinement for compounds **1** and **2** are summarized in Table 1.

Totals of 5483 (**1**) and 5738 (**2**) reflections were collected to a maximum 2θ value of 60.0°; 5218 (**1**) and 5368 (**2**) of them were unique, and from these, 1331 (**1**) and 1576 (**2**) were assumed as observed ($F_o > 3\sigma(F_o)$). For all these structures the data were corrected for Lorentz, polarization, and absorption effects. No decay correction was applied.

The structures of **1** and **2** were solved by heavy-atom Patterson methods[6] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on a DF map and refined isotropically. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.59 and -0.54 eÅ^{-3} (**1**), and 0.36 and -0.34 eÅ^{-3} (**2**), respectively. All calculations were performed using the teXsan[7] crystallographic software package. The final atomic coordinates of compounds **1** and **2** are given in Table 2 and Table 3, respectively.

RESULTS AND DISCUSSION

Structure of Complex 1

The syntheses of complexes **1** and **2** have been reported in the literature.[6] The crystal for X-ray crystal analysis of complex **1** can obtain to recrystallize from MeOH. An ORTEP view of complex **1** is shown in Figure 2 along with the numbering scheme. The selected bond distances and angles of complex **1** is given in Table 4.

TABLE 1 Crystallographic data for complexes **1** and **2**.

	1	**2**
formula	$C_{13}H_{24}N_7ClCuO_5$	$C_{17}H_{20}N_6CuO$
crystal system	monoclinic	monoclinic
fw	457.38	387.93
space group	$P2_1/n$	$P2_1/n$
a, Å	10.030(4)	7.338(4)
b, Å	12.393(5)	22.016(6)
c, Å	15.986(5)	11.169(4)
β, deg	95.59(3)	97.14(4)
V, Å^3	1977(1)	1790(1)
Z	4	4
ρ_{calc}, g/cm^{-1}	1.536	1.439
T, K	296	296
λ, Å	0.71069	0.71069
μ, cm^{-1}	12.79	12.38
no. of unique reflns	5218	5368
no. of reflns with (F > 3.0 σ (F))	1331	1576
R^a	0.067	0.047
$R_w{}^b$	0.073	0.053

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

The crystal of complex **1** consists of Cu(II) mononuclear complex cations of $[Cu(tacn)(Hbim)]^+$, perchlorate ions, and methanol molecules. The Cu(II) ion in complex **1** is bound at distorted square-pyramidal five nitrogens donor sets. The macrocyclic triamine is coordinated facially with N(5) and N(7) occupying equatorial positions and N(6) apically situated; N(2) and N(4) of $Hbim^-$ ligands are in the two remaining equatorial positions. The Cu-N lengths fall in range 2.01(1) - 2.23(1) Å, and Cu-N(6) [2.23(1) Å] apical distance is slightly long compared with those for other equatorial nitrogen atoms.

The equatorial Cu-N bonds are approximately equal [2.01(1)-2.02(1) Å] and compare well with the values reported for $Cu([9]aneN_3)Br_2$ [8] and $Cu([9]aneN_3)Cl_2$.[9] The apical Cu-N(6) distance [2.23(1) Å], while equal to that in $Cu([9]aneN_3)Br_2$ [2.23(4) Å] or slightly longer than that in $Cu([9]aneN_3)Cl_2$ [2.268(1) Å] and substantially longer than the equatorial Cu-N bonds may be anomalously shortened due to constraint by the macrocyclic triamine which causes the Cu-N (apical) bond to be tilted toward the basal N atoms. The perchlorate ion and the methanol molecule are free

TABLE 2 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) of complex **1**.

atom	x	y	z	B_{eq}
Cu	0.0384(2)	0.0773(1)	-0.2612(1)	3.11(3)
Cl	0.0885(4)	0.2882(3)	0.3347(2)	4.17(9)
O(1)	0.164(1)	0.3425(10)	0.2722(6)	6.1(3)
O(2)	-0.0470(10)	0.2633(8)	0.2999(6)	4.9(3)
O(3)	0.088(1)	0.3581(8)	0.4087(6)	5.2(3)
O(4)	0.155(1)	0.1838(9)	0.3590(7)	7.2(3)
O(5)	0.110(1)	0.345(1)	0.1044(8)	8.4(4)
N(1)	0.006(1)	0.3011(9)	-0.4465(6)	3.1(3)
N(2)	-0.010(1)	0.2112(9)	-0.3289(7)	3.4(3)
N(3)	0.1495(10)	0.081(1)	-0.4978(6)	3.4(3)
N(4)	0.113(1)	0.0353(9)	-0.3693(7)	3.5(3)
N(5)	0.059(2)	-0.068(1)	-0.2054(8)	5.8(4)
N(6)	0.209(1)	0.119(1)	-0.1661(7)	4.5(3)
N(7)	-0.072(1)	0.114(1)	-0.1662(8)	5.7(4)
C(1)	-0.063(1)	0.364(1)	-0.3941(10)	4.0(4)
C(2)	-0.074(1)	0.309(1)	-0.3229(8)	3.7(4)
C(3)	0.197(2)	-0.022(1)	-0.4831(10)	4.5(4)
C(4)	0.171(1)	-0.051(1)	-0.404(1)	4.1(4)
C(5)	0.034(1)	0.208(1)	-0.4045(7)	2.5(3)
C(6)	0.100(1)	0.113(1)	-0.4256(7)	2.8(3)
C(7)	0.194(3)	-0.080(2)	-0.157(1)	11.5(8)
C(8)	0.262(2)	0.013(2)	-0.140(2)	9.3(6)
C(9)	0.146(3)	0.182(2)	-0.101(1)	11.1(8)
C(10)	0.007(3)	0.180(2)	-0.102(1)	11.7(8)
C(11)	-0.114(2)	0.003(2)	-0.133(2)	11.4(7)
C(12)	-0.063(3)	-0.079(2)	-0.155(1)	11.6(8)
C(13)	-0.012(2)	0.404(2)	0.096(1)	10.4(7)

$B_{eq} = 8/3\{p^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos g + 2U_{13}aa^*cc^*\cos b + 2U_{23}bb^*cc^*\cos a)\}$

TABLE 3 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) of complex **2**.

atom	x	y	z	B_{eq}
Cu(1)	0.0772(1)	0.19599(4)	-0.02537(9)	2.54(2)
O(1)	0.2558(8)	0.2538(3)	-0.0691(6)	3.9(1)
N(1)	0.3343(9)	0.0428(3)	-0.1289(6)	3.1(2)
N(2)	0.1771(8)	0.1313(3)	-0.1203(5)	2.4(1)
N(3)	0.4317(10)	0.0580(3)	0.1454(6)	3.0(2)
N(4)	0.2571(9)	0.1405(3)	0.1277(6)	3.1(2)
N(5)	-0.1696(9)	0.1500(3)	-0.0203(6)	2.9(2)
N(6)	-0.0478(9)	0.2576(3)	-0.0616(6)	2.6(1)
C(1)	0.283(1)	0.0881(3)	-0.0598(7)	2.3(2)
C(2)	0.323(1)	0.0944(4)	0.0701(7)	2.5(2)
C(3)	0.160(1)	0.1114(4)	-0.2370(7)	2.8(2)
C(4)	0.254(1)	0.0590(4)	-0.2422(9)	3.4(2)
C(5)	0.331(1)	0.1326(5)	0.2453(8)	3.8(2)
C(6)	0.436(1)	0.0828(4)	0.2578(8)	3.8(2)
C(7)	-0.160(2)	0.0821(5)	-0.018(1)	5.1(3)
C(8)	-0.297(2)	0.1707(6)	-0.126(1)	4.9(3)
C(9)	-0.232(1)	0.1699(4)	0.0951(9)	3.6(2)
C(10)	-0.218(1)	0.2388(5)	0.1069(10)	3.9(2)
C(11)	0.003(1)	0.3137(4)	0.0777(7)	3.2(2)
C(12)	0.155(1)	0.3414(4)	0.0324(7)	3.2(2)
C(13)	0.273(1)	0.3110(4)	-0.0393(7)	3.0(2)
C(14)	0.415(1)	0.3444(4)	-0.0826(9)	3.9(2)
C(15)	0.436(2)	0.4058(4)	-0.0548(10)	4.5(2)
C(16)	0.325(2)	0.4355(4)	0.0150(9)	4.4(2)
C(17)	0.188(1)	0.4044(4)	0.0593(8)	4.0(2)

$B_{eq} = 8/3\{p^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos g + 2U_{13}aa^*cc^*\cos b + 2U_{23}bb^*cc^*\cos a)\}$

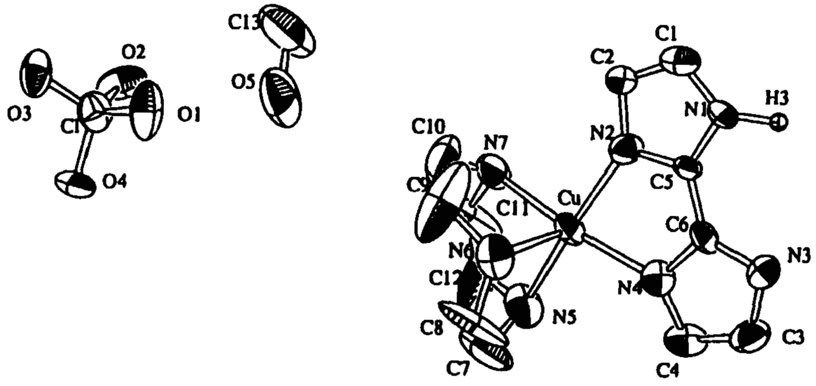

FIGURE 2 ORTEP view of complex **1**.

from the coordination and are captured in the crystal lattice with intermolecular hydrogen bonds. The perchlorate ion forms intermolecular hydrogen bonds with the NH groups of tacn [N(5)-O(2) 2.88(2); N(6)-O(2) 2.93(1); and N(7)-O(1) 2.78(2) Å] and Hbim$^-$.[N(1)-O(3) 2.63(1); and N(3)-O(4) 2.63(2) Å] in the [Cu(tacn)(Hbim)]$^+$ cation. It should be noted that the two hydrogen atoms of H(1) and H(2) of Hbim$^-$ are in disorder with 0.5 occupancy factors, respectively. The methanol molecule forms the hydrogen bond between perchlorate ion [O(5)-O(1) 2.68 Å].

Structure of Complex 2

In order to preclude an interaction with the counter anion and to construct the hydrogen bonded dimer (Figure 1), we chose the mononegative, tridentate ligand N-salicylidene-N',N'-dimethylethylenediamine (salenNMe$_2$) in place of the neutral, triazamacrocycle ligand. Thus, a neutral complex of copper(II) with Hbim$^-$ and salenNMe$_2$, [Cu(salenNMe$_2$)(Hbim)]$_2$ (**2**), was designed and synthesized.

In this system, the tridentate ligand cannot donate a hydrogen bond and the methyl groups suppress the coordination of a solvent molecule to axial coordination positions.[10] However, an equatorial coordination position is available for binding to the Hbim$^-$ ligand.An ORTEP view of complex **2** is shown in Figure 3 along with the numbering scheme. The selected bond distances and angles of complex **2** are given in Table 5.

The crystal structure is comprised of only mononuclear Cu(II) complex units; [Cu(salenNMe$_2$)(Hbim)]. The primary coordination sphere is pseudo-square pyramidal with the tridentate Schiff base [Cu(1)-O(1) 1.933(6); Cu(1)-N(6) 1.962(6); Cu(1)-N(5) 2.082(6) Å] and N(2) of the Hbim$^-$ monoanion [Cu(1)-N(2) 1.970(6) Å] defining

TABLE 4 Selected bond lengths (Å) and angles (deg) for compound **1**[a].

Distances			
Cu - N(2)	2.01(1)	Cu - N(4)	2.02(1)
Cu - N(5)	2.02(1)	Cu - N(6)	2.23(1)
Cu - N(7)	2.02(1)	N(1) - C(1)	1.38(2)
Cu - C(2)	1.34(2)	N(2) - C(2)	1.38(2)
N(2) - C(5)	1.33(1)	N(1) - C(5)	1.35(1)
N(4) - C(4)	1.36(2)	C(4) - C(3)	1.36(2)
N(3) - C(3)	1.37(2)	N(3) - C(6)	1.36(1)
N(4) - C(6)	1.32(2)	C(5) - C(6)	1.41(2)
Angles			
N(2) - Cu - N(4)	80.9(4)	N(2) - Cu - N(5)	169.9(5)
N(2) - Cu - N(6)	107.7(5)	N(2) - Cu - N(7)	95.5(5)
N(4) - Cu - N(5)	96.8(5)	N(4) - Cu - N(6)	108.7(4)
N(4) - Cu - N(7)	168.4(5)	N(5) - Cu - N(6)	82.4(5)
N(5) - Cu - N(7)	84.8(6)	N(6) - Cu - N(7)	82.9(3)

[a] Estimated standard deviations are given in parentheses.

the equatorial plane and N(4) of the coordinated Hbim$^-$ ligand occupying one of the axial positions [Cu(1)-N(4) 2.365(7) Å]. The Hbim$^-$ ligand acts as a chelated ligand employing both equatorial and axial ligations. In copper(II) complexes with this salenNMe$_2$ and the ligand with similar coordination modes, only two complexes; [Cu(salenNMe$_2$)(theopyllinato)][10] and [Cu(BsalenNMe$_2$)(theopyllinato)] (BsalenNMe$_2$ =N-3,4-benzosalicylidene-N.N'-dimethylethylenediamine),[11] were already revealed their structures by X-ray crystal analysis. [Cu(BsalenNMe$_2$)(theopyllinato)], has a pseudo-square pyramidal similar to that of complex **2**.

The most important intermolecular interaction found in the crystal packing is formation of the dimeric H-bonding [N(1)-N(3) 2.83(10) Å] of a NH...N type between the Hbim$^-$ ligands. The two Hbim$^-$ skeletons connected by the double NH...N type hydrogen bonds exist on a coplanar.

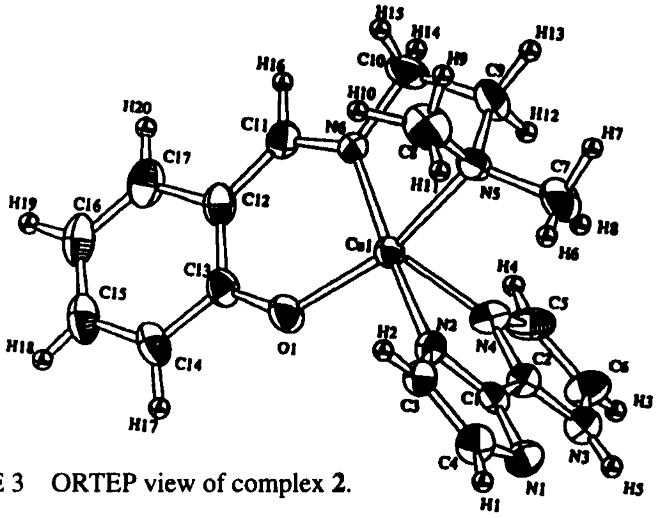

FIGURE 3 ORTEP view of complex 2.

TABLE 5. Selected bond lengths (Å) and angles (deg) for compound 2[a].

Distances			
Cu(1) - O(1)	1.933(6)	Cu(1) - N(2)	1.970(6)
Cu(1) - N(4)	2.365(7)	Cu(1) - N(5)	2.082(6)
Cu(1) - N(6)	1.962(6)	N(1) - C(1)	1.344(9)
N(1) - C(4)	1.38(1)	C(4) - C(3)	1.35(1)
C(3) - N(2)	1.366(10)	N(2) - C(1)	1.355(10)
N(4) - C(2)	1.327(9)	C(2) - N(3)	1.348(10)
N(3) - C(6)	1.36(1)	C(6) - C(5)	1.34(1)
C(1) - C(2)	1.45(1)		

Angles			
O(1) - Cu(1) - N(2)	91.8(2)	O(1) - Cu(1) - N(4)	100.8(3)
O(1) - Cu(1) - N(5)	161.2(3)	O(1) - Cu(1) - N(6)	92.5(3)
N(2) - Cu(1) - N(4)	78.7(2)	N(2) - Cu(1) - N(5)	92.7(3)
N(2) - Cu(1) - N(6)	174.0(3)	N(4) - Cu(1) - N(5)	98.0(2)
N(4) - Cu(1) - N(6)	104.6(2)	N(5) - Cu(1) - N(6)	82.0(3)

[a] Estimated standard deviations are given in parentheses.

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