Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Architectures Based on Hydrogen Bond and Coordination Bond Toward New Functionality

Kazuhiro Nakasuji [a], Makoto Tadokoro [b], Jiro Toyoda [a], Minoru Mitsumi [c], Tetsuji Itoh [c] & Kenji Iijima [a]

[a] Department of Chemistry, Faculty of Science, Osaka University Toyonaka, Osaka, 560, Japan

[b] Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

[c] Department of Structural Molecular Science, The Graduate University for Advanced Studies, Myodaiji, Okazaki, 444, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Kazuhiro Nakasuji , Makoto Tadokoro , Jiro Toyoda , Minoru Mitsumi , Tetsuji Itoh & Kenji Iijima (1996): Molecular Architectures Based on Hydrogen Bond and Coordination Bond Toward New Functionality, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 285:1, 241-248

To link to this article: http://dx.doi.org/10.1080/10587259608030808

Mol. Cryst. Liq. Cryst., 1996, Vol. 285, pp. 241–248
Reprints available directly from the publisher
Photocopying permitted by license only

MOLECULAR ARCHITECTURES BASED ON HYDROGEN BOND AND COORDINATION BOND TOWARD NEW FUNCTIONALITY

KAZUHIRO NAKASUJI,[a] MAKOTO TADOKORO,[b] JIRO TOYODA,[a]
MINORU MITSUMI,[c] TETSUJI ITOH,[c] and KENJI IIJIMA[a]

[a] Department of Chemistry, Faculty of Science, Osaka University
Toyonaka. Osaka 560, Japan

[b] Department of Chemistry, Faculty of Science, Osaka City University
Sumiyoshi-ku, Osaka 558, Japan

[c] Department of Structural Molecular Science, The Graduate University for
Advanced Studies, Myodaiji, Okazaki 444, Japan

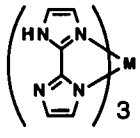
Abstract we report the design of new molecular building blocks with hydrogen-bonding sites and the production of a variety of molecular architectures by hydrogen-bonds and coordination bonds. We selected the ligands, such as biimidazole, pterine, lumazine, and glyoxime which have chelating ability to a metal element and multi-hydrogen-bonding sites.

INTRODUCTION

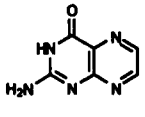
An unique intermolecular force in the strength, directionality, and complementarity of hydrogen-bonding (H-bonding) plays a central role in designing and creating a variety of molecular architectures for molecular self-assembly and molecular recognition in chemical, physical, and biological sciences.[1–3] Crystal engineering contributes to progress such sciences and makes possible to produce long-range ordered H-bonded systems such as one-, two-, and three-dimensional (1D, 2D, and 3D) molecular architectures in a predictable fashion. In addition, cooperative interaction of H-bonding with electron in conjugated electronic systems is an unique aspects to explore new molecular materials with interesting solid state properties.[4] The coordination bonds between a transition metal and a ligand can also be used to produce such molecular architectures.[5]

In this report, we present the design of new molecular building blocks with H-bonding sites and the production of a variety of molecular architectures by H-bonds and coordination bonds. We selected the ligands, such as biimidazole, pterine, lumazine, and glyoxime which have chelating ability to a metal element and multi-H-bonding sites.

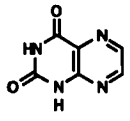
Tris-biimidazolate nickel complex (**1**) as a molecular block forms a variety of crystal structures of 1D and 2D H-bonding networks, in which an unprecidented example of an infinite self-assembly, that is, cross-catenated structure of two sheets of the extended hexagonal 2D networks is included.[6] Crystal structures of pterine (**2**) and lumazine (**3**) metal complexes showed 3D H-bonded networks and stacking interactions between the π-electron systems.[7] Ethylenediaminoglyoxime metal (**4**) complexes gave highly conducting charge-transfer complexes with TCNQ having 2D H-bonded networks.[5a]



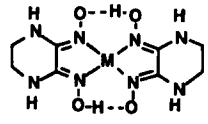
1



2



3



4

RESULTS AND DISCUSSION

1. Tris-biimidazolate Nickel (II) Complexes (**1**)

2,2'-Biimidazolate ($Hbim^-$) ligand has an ability to form coordination bonds by chelation and multi-point H-bonds. The transition metal complexes with three bidentate $Hbim^-$ ligands, tris-biimidazolate Nickel (II) complexes (**1**), can construct a three-dimensional H-bonded networks by using the complementary H-bonding sites. We have found that the Ni(II) complexes ($[Ni(Hbim)_3]^-$) form a variety of crystal structure (**1a** – **1c**) with intermolecular H-bonded networks depending on the kind of the counter cations.

(1) $[Ni(Hbim)_3](n\text{-}Pr_4N)$-MeOH (**1a**)

The crystal structure of compound **1a** consists of the enantiomers of Δ and Λ of tris-biimidazolate ($[Ni(Hbim)_3]^-$), counter cations ($n\text{-}Pr_4N^+$), and methanol molecules. The $[Ni(Hbim)_3]^-$ complex has an approximate point group D_3 symmetry and contains the Λ and Δ isomers as shown in Figure 1. The $n\text{-}Pr_4N^+$ cations and the methanol molecules are free from the coordination to metal ion. The characteristic feature found in the crystal packing is the formation of a zigzag ribbon structure with intermolecular H-bonds of two NH···N types of imidazole ligands, as shown in Figure 2. The ribbon structures are made up of an alternate arrangement of Δ and Λ enamtiomers of the Ni(II) anion. The other remaining $Hbim^-$ ligand does not participate in such H-bonding chains and has

an H-bonding interaction with methanol.

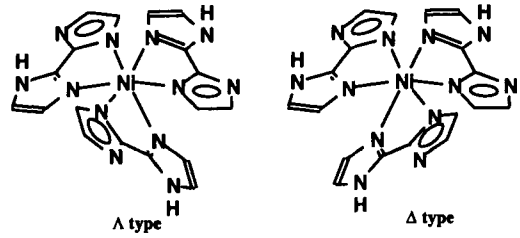


FIGURE 1 Tris-biimidazolate nickel (II) complex, $[Ni(Hbim)_3]^-$.

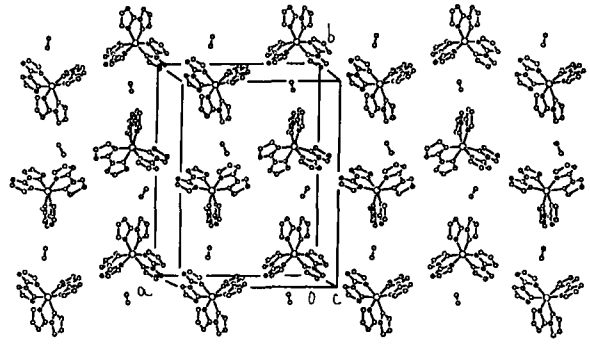


FIGURE 2 Structure of one-dimensional zigzag chain of complex **1a**.

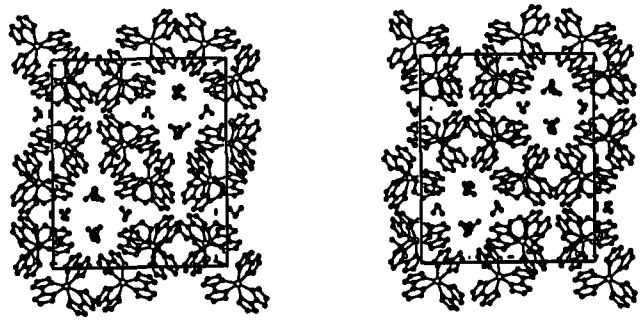


FIGURE 3 Packing structure of complex **1b** on the *ab* plane.

(2) $[Ni(Hbim)_3](PTMA)$-3MeOH (**1b**)

The crystal structure of the complex **1b** consists of the Δ and Λ enantiomers of $[Ni(Hbim)_3]^-$, phenyltrimethyl ammonium cations ($PTMA^+$), and methanol molecules (Figure 3). Four $[Ni(Hbim)_3]^-$ and four PTMA cations form a ring structure with cavity. The ring structures produce the channel structures by stacking along the *c* axis. The inside of the channel is hydrophilic and filled by the H-bonded methanols. The complex $[Ni(Hbim)_3]^-$ is linked each other to form the dimer arrangement by a direct H-bonding of NH···N types between the same optical isomers.

(3) $[Ni(Hbim)_3]_2(NEt_4)_2(Hbim)$-MeOH (**1c**)

The crystal structure of the complex **1c** has four characteristic points (Figure 4). First, the complex has an one-dimensional zigzag ribbon structure by intermolecular H-bonds similar to the structure described in the complex **1a**. The ribbon structure is comprised of the alternate arrangement of Δ and Λ enamtiomers of the complex $[Ni(Hbim)_3]^-$. Second, free biimidazole molecule (H_2bim) connects the one-dimensional zigzag ribbons by the intermolecular H-bonds to form hexagonal networks. Third, the two pairs of the honeycomb sheets perpendicularly oriented form a cross-catenated structure. Finally, such a cross-catenated structure expands to three-dimension to form an infinite cross-catenated structure.

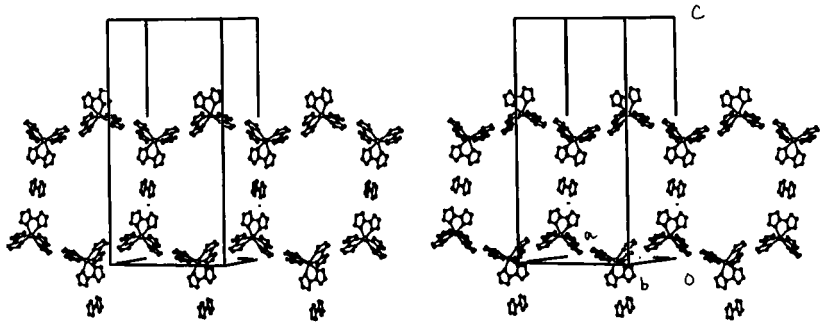
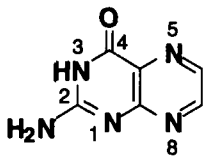


FIGURE 4 Crystal structure of conplex **1c**

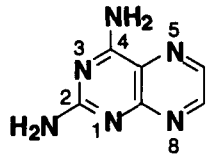
2. Mononuclear Copper(II)–Pteridine Complex **2**

In principle, CT interaction can be related to the redox properties of the metal atoms and/or the stacking interactions between the ligands. In order to study the basic chemistry of such systems, we need to construct metallosupramolecular systems in which ligands are connected by intermolecular H-bonds. As a basic skeleton of the ligands, we have utilized the pteridine derivatives, such as pterin (HPR) and 2,4-diaminopteridine

(DAP), which have the ability to chelate to metal atoms and H-bonding sites of NH···O and NH···N types in the solid state. Here, we report the crystal structure of the complex, $[Cu(PR)_2(H_2O)_2]\,2H_2O$ (**2**).[7]



HPR



DAP

The complex **2** possesses an inversion center (Figure 5). The coordination sphere of copper(1) atom has an elongated octahedral coordination geometry defined by two N atoms and two O atoms of PR ligands lying in the equatorial plane and by two water molecules at apexes. The dihedral angle between the plane formed by O, Cu, and N atoms and the ligand PR plane is 13.11°, and the Cu atom deviates by 0.36 Å from the plane of the ligand PR. Packing diagrams of **2** is presented in Figure 6. In **2**, the noncoordinated water molecules are involved in a three-dimensional H-bonded network. The molecular units of **2** are linked into a two-dimensional molecular sheet parallel to the *ab* plane via H-bonds among PR, coordinated and noncoordinated water molecules. The molecular sheets are further linked to each other through double H-bonds between molecular units to form a three-dimensional H-bonded network. In the sheet, there are two types of PR stacking along the *a*-axis with the alternated distances of 3.25 and 3.20 Å, respectively.

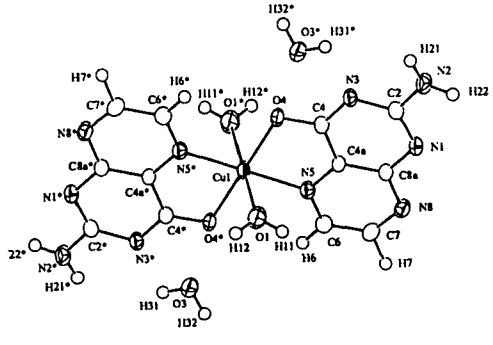


FIGURE 5 ORTEP diagram for **2**.

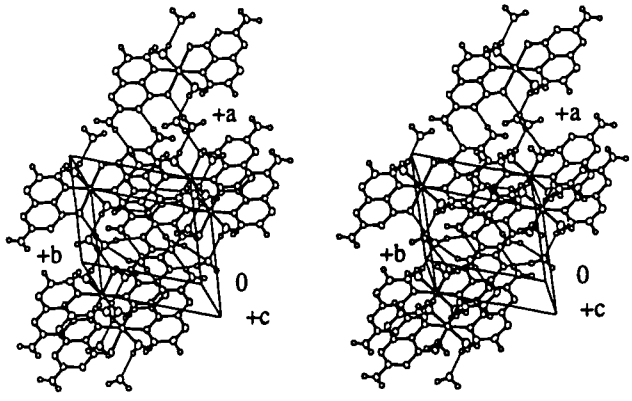


FIGURE 6 Stereoview of **2** showing three-dimensional H-bonded network.

3. Ethylenediaminoglyomimato palladium(II)–TCNQ (**4**–TCNQ)

The H-bonded charge-transfer (CT) systems (the HBCT systems), which exhibit cooperative interaction between H-bonding and CT, can be a good candidate for new molecular materials having interesting solid state properties.[4] Generally, the solid state properties of the HBCT systems depend on the degree and cooperativity of H-bonding and CT. Endres and his coworkers have reported good examples of HBCT system, that is, CT complexes of (diaminoglyoximato)(diaminoglyoxime)transition metal complex with TCNQ, M(Hdag)(H_2dag)·TCNQ, which showed highly electrical conductivity.[8] In order to accumulate a variety of such examples and to develop our idea, we have modified the diaminoglyoxime (Hdag) ligand. Here, we describe the crystal structure of a HBCT system having the reduced number of H-bonds, that is, (ethlenediaminoglyoximato)(ethylenediaminoglyoxime)palladium(II) **4** with TCNQ, Pd(Hedag)-(H_2edag)·TCNQ.[5a]

The complex of (ethlenediaminoglyomimato)(ethylenediaminoglyoxime)-palladium(II) **4**·TCNQ crystallizes in the triclinic and the space group $P\bar{1}$. The crystal structure indicates that the cationic component of the palladium complex and the anionic component of TCNQ are arranged in uniform, segregated stacking mode along the *c* axis (Figure 7). The O···O distance of the intramolecular H-bonds in oxime moiety is 2.94(1) Å. The other hydrogen atom on the oxime is in a positional disorder and form intermolecular H-bond (2.61(1) Å) to the adjacent transition metal column. The

intermolecular H-bonding interactions between the cationic transition metal and the anionic TCNQ components of **4**·TCNQ are more simple compared with those of M(Hdag)(H_2dag)·TCNQ.[9] Thus, the cationic and anionic components are linked via one kind of intermolecular H-bonding between NH of the amino group and N of the nitrile group (2.94(1) Å). The cationic stacks are linked to sheet via one kind of intermolecular H-bonding between the oxime oxygen involving the disordered H atom.

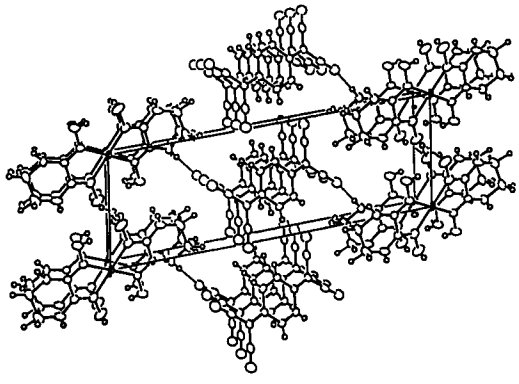


FIGURE 7 Crystal structure of **4**·TCNQ.

We estimated the degree of CT for **4**·TCNQ to be 0.70 and 0.67 by using the nitrile stretching frequency and by the bond length ratio procedure of TCNQ skeleton, respectively. As mentioned, the formal charge of the TCNQ skeleton for the complex **4**·TCNQ is one. The reason of the discrepancy between the estimated values and the formal charge is not clear at this stage, but the H-bonding interaction between NH of the amino group and N of the nitrile group might reduce the ionicity to a some extent. We observed a broad absorption band around 3300 cm^{-1}, which can be assigned to the intra band CT transition in the TCNQ column with a partial ionicity. The electrical conductivity for a single crystal of the complex **5**·TCNQ gave 90 Scm^{-1} with metallic behavior around room temperature. Such a highly conducting behavior is consistent with the partial ionicity estimated and the existence of the intra-band CT transition.

This work was partially supported by The Grant-in-Aid for Scientific Research from Ministry of Education, Science and Culture of Japan and the grant of Yamada Science Foundation.

EFERENCE

1. X. Wang, M. Simard and J. D. Wuest, *J. Am. Chem. Soc.*, **116**, 12119 (1994).
2. S. Subramanian and M. J. Zaworotko, *Coord. Chem. Rev.*, **137**, 357 (1994).
3. J. C. MacDonald and G. M. Whitesides, *Chem. Rev.*, **94**, 2383 (1994).
4. K. Nakasuji, K. Sugiura, T. Kitagawa, J. Toyoda, H. Okamoto, K. Okaniwa, T. Mitani, H. Yamamoto, I. Murata, A. Kawamoto, and J. Tanaka, *J. Am. Chem. Soc.*, **113**,1862 (1991).
5. a) T. Itoh, J. Toyoda, M. Tadokoro, H. Kitagawa, T. Mitani, and K. Nakasuji, *Chem. Lett.*, **1995**, 41-42. b) M. Tadokoro, J. Toyoda, K. Isobe, T. Itoh, A. Miyazaki, T. Enoki, and K. Nakasuji, *Chem. Lett.*, **1995**, 613-614.
6. M. Mitumi, J. Toyoda, and K. Nakasuji, *Inorg. Chem.*, **34**, 3367-3370 (1995).
7. M. Tadokoro, K. Isobe, and K. Nakasuji, *Mol. Cryst. Liq. Cryst.*, **278**, 221-224 (1996).
8. H. Endress, A. Bongart, D. Nothe, I. Henning, D. Schweitzer, H. Schafer, H. W. Helberg, and S. Flandrois, *Z. Naturforsch.*, **40b**, 489, (1985).
9. H. Endress, *Angew. Chem., Int. Ed. Engl.*, **21**, 524 (1982).