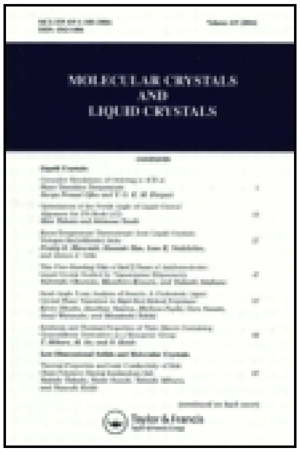


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

One-Dimensional Solid State Structures with a New "ΔΔ-ΔΔ" Arrangements of "Crinkled Ribbon" Derived from Cis Dibiimidazolate Ni(Ii) Complexes

Makoto Tadokoro [a] , Makiko Daigo [a] , Kiyoshi Isobe [b] , Keiji Matsumoto [a] & Kazuhiro Nakasuji [c]

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

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

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

Version of record first published: 04 Oct 2006

To cite this article: Makoto Tadokoro, Makiko Daigo, Kiyoshi Isobe, Keiji Matsumoto & Kazuhiro Nakasuji (1997): One-Dimensional Solid State Structures with a New "ΔΔ-ΔΔ" Arrangements of "Crinkled Ribbon" Derived from Cis Dibiimidazolate Ni(Ii) Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 41-47

To link to this article: http://dx.doi.org/10.1080/10587259708044547

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 41–47
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published under license
in The Netherlands under the Gordon and Breach
Science Publishers imprint
Printed in India

ONE-DIMENSIONAL SOLID STATE STRUCTURES WITH A NEW "ΔΔ-ΛΛ" ARRANGEMENTS OF "CRINKLED RIBBON" DERIVED FROM CIS-DIBIIMIDAZOLATE Ni(II) COMPLEXES

MAKOTO TADOKORO[1], MAKIKO DAIGO[1], KIYOSHI ISOBE[2], KEIJI MATSUMOTO[1] AND KAZUHIRO NAKASUJI[3]
Department of Chemistry[1] and Department of Material Science,[2] Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan; Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan[3]

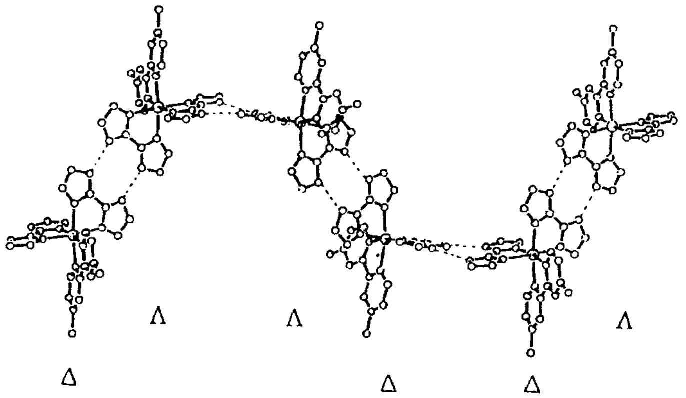
Abstract The nickel complex of *cis*-[Ni(Hbim)$_2$(Me$_2$bpy)] (Hbim = 2,2'-biimidazolate monoanion; Me$_2$bpy = 4,4'-dimethyl-2,2'-dipyridine) (1) is synthesized and its crystal structure is characterized by X-ray crystal analysis (Crystal data: *monoclinic*, $P2_1/n$ (No. 14), a = 14.03(1) Å, b = 15.97(1) Å, c = 24.382(3) Å, β = 101.24(4)°, V = 5358(5) Å^3, Z = 8). The crystal structure comprises assemblies of one-dimensional crinkled-ribbon structures built up by an alternate arrangement of ΔΔ and ΛΛ binary optical isomers of the building block 1. The crinkled-ribbon format is formed by complementary intermolecular hydrogen bonds of Hbim ligands in the building block 1. In crystal, the crinkled-ribbon structure includes free ligands of Me$_2$bpy.

INTRODUCTION

We are interested in three subjects in the solid state crystal with transition metal complexes, (1) rationalizing the crystal structures engineering through the control of the structures of their component building blocks of metal complexes, (2) predicting the crystal structures of new molecular building blocks; and (3) designing molecular based building blocks that crystallize in designed arrays.[1] An understanding of intermolecular interactions that is sufficiently detailed to accomplish these properties would be useful throughout material science and would contribute to molecular recognition and molecular self-assembly. In general the problem of understanding and predicting the packing of metal complexes in crystals is complicated: a number of possible arrangements of molecules in the crystal need to be considered, the differences in energy between crystal forms may be small, and there are no easy methods to identify the most stable of these forms.[2,3]

In the previous paper, we can simplify the problem by reducing the number of orientations open to each molecule by forcing them to form "zigzag ribbons" connected by networks of intermolecular hydrogen bonds with one-dimensional chain arrangements.[4] Packing of hydrogen bonded zigzag ribbons would necessarily limit their constituent molecules to a set of arrangements in space that is substantially reduced relative to that available to molecules without constraints on their packing. We have already described a solid-state structure based on a "zigzag-ribbon" motif constructed from the alternate arrangement of enantiomers of the Δ and Λ types to repeat the ΔΛ ΔΛ ΔΛ ··· sequence of *cis*-[Ni(Hbim)$_2$(L)] building blocks (L = some bidentate chelate ligands).[4] The zigzag ribbon motif was comprised from complementary binary NH-N hydrogen bonds of 2,2'-biimidazolate metal complexes as the building block .

We have found that steric properties of the substituents on the L ligands leads to the selective formation change in other sequence of the Δ and Λ optical isomers of the*cis*-[Ni(Hbim)$_2$(L)] building blocks. Here we report solid-state structures of a new type of "crinkled-ribbon" format in a ΔΔ ΛΛ ΔΔ ΛΛ ··· sequence, obtained by combination of the Δ and Λ enantiomers of *cis*-[Ni(Hbim)$_2$(Me$_2$bpy)]) (Me$_2$bpy = 4,7-dimethyl-2,2'-dipyridine) building blocks, as shown Figure 1.



FUGURE 1 The crystal structure of one-dimensional "crinkled-ribbon" with ΔΔ–ΛΛ arrangements of the building block **1**.

EXPELIMENTALS

Preparation

The synthetic method of the building block *cis*-[Ni(Hbim)$_2$(Me$_2$bpy)] (**1**) was performed by the procedure of a 'one-pot' self-assembly similar to that used for the construction of the array of *cis*-[Ni(Hbim)$_2$(en)].[4] Complex **1** made from the new building block was obtained by refluxing the mixture of the dissolved 2,2'-biimidazole (H$_2$bim) (2 mmol), 4,4'-dimethyl-2,2'-dipyridine (1 mmol) and 28 % NaOMe methanol solution (1.5 g) in MeOH (30 cm^3) followed by the addition of the methanol solution (40 cm^3) of Ni(ClO$_4$)$_2$·6H$_2$O (1 mmol). The reaction mixture was heated for 30 minutes and filtered. The filtrate was concentrated to ca. 40 cm^3 and cooled slowly to room temperature and left over night. First, a small amount of orange-yellow crystal was formed and separated. Second, the resulting crystalline solid was precipitated from remaining filtrate. The micro crystalline solid was filtered and air dried. In suitable for single-crystal X-ray diffraction studies were extracted from the first precipitate. Elemental analysis supported from the second micro crystalline solids. (Analysis of *cis*-[Ni(Hbim)$_2$(Me$_2$bpy))]; C$_{24}$H$_{22}$N$_{10}$Ni; Found: C, 27.12%; H, 4.31%; N, 27.12%, Calcd: C, 55.83%; H, 4.35%; N, 27.51%)

Crystal Structure

The crystal data of [Ni(Hbim)$_2$(dmbpy)]1/2(dmbpy) (**1**) is formula, C$_{30}$H$_{27}$N$_{22}$Ni, *monoclinic*, space group *P*21/c (No. 14), *FW* = 600.32, a = 14.03(1) Å, b = 15.97(1) Å, c = 24.382(3) Å, β = 101.24(4)°, V = 5358(5) Å^3, Z = 8, ρ_{calc} = 1.310 g/cm^{-1}, Mo-Kα radiation, λ = 0.71069 Å, $6.0 < 2\theta < 50°$, 9818 reflections were collected, of which 3876 unique reflections ($I > 3\sigma(I)$) were used for refinement (639 parameters), converging to R = 0.056 and R_w = 0.079. The structure of complex **1** was solved by heavy-atom Patterson methods[5] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed in calculation. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.32 eÅ^{-3}. All calculations were performed using the teXsan[6] crystallographic software package. The selected bond distances and angles of complex **1** is given in Table 1. The final atomic coordinates of complex **1** are given in Table 2.

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

Distances

Ni(1) - N(1)	2.088(6)	Ni(1) - N(3)	2.059(6)
Ni(1) - N(5)	2.094(6)	Ni(1) - N(7)	2.074(6)
Ni(1) - N(9)	2.069(6)	Ni(1) - N(10)	2.100(6)
Ni(2) - N(11)	2.096(5)	Ni(2) - N(13)	2.091(5)
Ni(2) - N(15)	2.068(6)	Ni(2) - N(17)	2.099(5)
Ni(2) - N(19)	2.080(5)	Ni(2) - N(20)	2.093(6)

Angles

N(1) - Ni(1) - N(3)	78.8(2)	N(1) - Ni(1) - N(5)	96.2(2)
N(1) - Ni(1) - N(7)	168.8(2)	N(1) - Ni(1) - N(9)	98.1(2)
N(1) - Ni(1) - N(10)	91.3(2)	N(3) - Ni(1) - N(5)	95.3(2)
N(3) - Ni(1) N(7)	90.8(2)	N(3) - Ni(1) - N(9)	170.9(2)
N(3) - Ni(1) - N(10)	94.0(2)	N(5) - Ni(1) - N(7)	80.6(2)
N(5) - Ni(1) - N(9)	93.5(2)	N(5) - Ni(1) - N(10)	169.0(2)
N(7) - Ni(1) - N(9)	92.9(2)	N(7) - Ni(1) - N(10)	93.6(2)
N(9) - Ni(1) - N(10)	77.5(2)	N(11) - Ni(2) - N(13)	79.3(2)
N(11) - Ni(2) - N(15)	89.8(2)	N(11) - Ni(2) - N(17)	168.1(2)
N(11) - Ni(2) - N(19)	97.2(2)	N(11) - Ni(2) - N(20)	99.1(2)
N(13) - Ni(2) - N(15)	91.4(2)	N(13) - Ni(2) - N(17)	95.9(2)
N(13) - Ni(2) - N(19)	171.9(2)	N(13) - Ni(2) - N(20)	95.1(2)
N(15) - Ni(2) - N(17)	79.4(2)	N(15) - Ni(2) - N(19)	95.9(2)
N(15) - Ni(2) - N(20)	169.7(2)	N(17) - Ni(2) - N(19)	89.0(2)
N(17) - Ni(2) - N(20)	92.1(2)	N(19) - Ni(2) - N(20)	78.1(2)

---

[a] Estimated standard deviations are given in parentheses.

RESULTS AND DISCUSSION

Crystal Structure of Complex 1

In Figure 1, the X-ray crystal structure of **1** shows that the desired coordination and aggregation has been achieved in the extended array of the nickel atom being coordinated to two Hbim$^-$ and L ligands as *cis*-isomers, which are in turn involved in an binary NH-N hydrogen bond arrangements with the other same building block. The crystal of complex **1** consists of Δ and Λ optical isomers of the *cis*-biimidazolate mononuclear Ni(II) complex with the ligand of 4,4'-dimethyl-2,2'-dipyridine (*cis*-[Ni(Hbim)$_2$(Me$_2$bpy)]), and the free ligand of 4,4'-dimethyl-2,2'-dipyridine.

The most important interaction found in the crystal structure of the building block is intermolecular hydrogen bonds to form one-dimensional crinkled ribbon structures. The crinkled ribbon structures are built up by the complementary hydrogen bonds of NH-N type between the alternate arrangement of ΔΔ and ΛΛ optical isomers : N(6)*-N(8): 2.75 Å; N(12)-N(14)*: 2.77 Å. Each pair of ΔΔ and ΛΛ optical isomers are also formed

TABLE 2 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

atom	x	y	z	B_{eq}
Ni(1)	0.09325(7)	0.31650(6)	0.67758(4)	6.14(2)
Ni(2)	0.56816(7)	0.21460(6)	0.91438(4)	5.29(2)
N(1)	0.0821(5)	0.3238(4)	0.7616(2)	6.7(2)
N(2)	-0.0176(5)	0.3006(4)	0.8231(3)	6.9(2)
N(3)	-0.0498(4)	0.2834(4)	0.6733(3)	6.8(2)
N(4)	-0.1633(4)	0.2404(4)	0.7169(3)	7.1(2)
N(5)	0.0646(4)	0.4432(4)	0.6592(2)	6.2(2)
N(6)	0.0302(4)	0.5363(4)	0.5905(2)	6.6(2)
N(7)	0.0751(4)	0.3119(4)	0.5911(2)	6.1(2)
N(8)	0.0243(5)	0.3821(4)	0.5100(2)	6.6(2)
N(9)	0.2421(4)	0.3316(4)	0.6880(2)	5.7(1)
N(10)	0.1442(4)	0.1928(3)	0.6881(2)	6.3(2)
N(11)	0.5560(4)	0.2684(3)	0.9911(2)	5.6(1)
N(12)	0.5340(5)	0.3893(4)	1.0359(2)	8.1(2)
N(13)	0.5003(4)	0.3280(3)	0.8875(2)	5.8(1)
N(14)	0.4676(6)	0.4560(4)	0.9129(2)	8.6(2)
N(15)	0.7043(4)	0.2679(4)	0.9209(2)	6.3(2)
N(16)	0.8338(4)	0.2885(4)	0.8832(2)	6.1(2)
N(17)	0.6004(4)	0.1812(3)	0.8368(2)	5.5(1)
N(18)	0.7157(4)	0.1835(4)	0.7841(2)	6.2(2)
N(19)	0.6177(4)	0.0977(3)	0.9452(2)	5.3(1)
N(20)	0.4400(4)	0.1440(3)	0.8995(2)	5.3(1)
N(21)	0.9484	0.0286	0.5646	19.3(4)
C(1)	0.1313(5)	0.3422(5)	0.8131(3)	7.3(2)
C(2)	0.0712(7)	0.3285(6)	0.8502(3)	8.3(3)
C(3)	-0.1289(6)	0.2524(6)	0.6343(3)	7.8(2)
C(4)	-0.1977(6)	0.2265(6)	0.6620(4)	8.6(3)
C(5)	-0.0049(5)	0.2992(4)	0.7703(3)	6.0(2)
C(6)	-0.0748(5)	0.2748(5)	0.7222(3)	6.2(2)
C(7)	0.0598(6)	0.5204(5)	0.6818(3)	7.3(2)
C(8)	0.0394(6)	0.5784(5)	0.6410(3)	7.4(2)
C(9)	0.0673(6)	0.2579(5)	0.5484(4)	7.4(2)
C(10)	0.0369(6)	0.3003(5)	0.4987(3)	7.4(2)
C(11)	0.0466(5)	0.4553(4)	0.6031(3)	6.2(2)
C(12)	0.0466(5)	0.3849(4)	0.5662(3)	5.6(2)
C(13)	0.2906(6)	0.4046(4)	0.6880(3)	6.4(2)
C(14)	0.3892(6)	0.4083(5)	0.6882(3)	6.2(2)
C(15)	0.4422(5)	0.3360(5)	0.6895(3)	6.0(2)
C(16)	0.3949(5)	0.2617(5)	0.6904(3)	6.0(2)
C(17)	0.2952(5)	0.2607(5)	0.6901(3)	5.6(2)
C(18)	0.5491(6)	0.3381(6)	0.6917(3)	8.7(3)
C(19)	0.0907(6)	0.1243(6)	0.6895(4)	8.1(3)
C(20)	0.1300(8)	0.0442(5)	0.6944(4)	9.6(3)

TABLE 2 Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) (continued).

atom	x	y	z	B_{eq}
C(21)	0.2285(7)	0.0320(6)	0.6988(5)	10.0(3)
C(22)	0.2799(6)	0.1033(5)	0.6978(4)	8.2(2)
C(23)	0.2380(6)	0.1821(5)	0.6914(3)	6.2(2)
C(24)	0.2705(8)	-0.0528(6)	0.7037(6)	16.1(4)
C(25)	0.5831(6)	0.2574(5)	1.0483(3)	7.0(2)
C(26)	0.5672(7)	0.3295(5)	1.0745(3)	8.2(2)
C(27)	0.4680(7)	0.3744(5)	0.8403(3)	7.8(2)
C(28)	0.4463(7)	0.4517(5)	0.8544(3)	9.3(3)
C(29)	0.5287(6)	0.3477(4)	0.9871(3)	6.1(2)
C(30)	0.4973(6)	0.3790(4)	0.9298(3)	6.2(2)
C(31)	0.7706(6)	0.3158(5)	0.9577(3)	7.1(2)
C(32)	0.8486(6)	0.3270(5)	0.9342(3)	7.6(2)
C(33)	0.5663(5)	0.1374(4)	0.7894(3)	6.2(2)
C(34)	0.6370(6)	0.1396(5)	0.7571(3)	7.1(2)
C(35)	0.7456(5)	0.2537(4)	0.8775(3)	5.2(2)
C(36)	0.6882(5)	0.2065(4)	0.8307(3)	5.3(2)
C(37)	0.7112(6)	0.0766(5)	0.9652(3)	6.6(2)
C(38)	0.7419(6)	-0.0055(5)	0.9763(3)	6.9(2)
C(39)	0.6723(6)	-0.0695(5)	0.9677(3)	6.8(2)
C(40)	0.5757(5)	-0.0474(4)	0.9476(3)	6.0(2)
C(41)	0.5507(5)	0.0359(4)	0.9363(2)	4.9(2)
C(42)	0.7009(7)	-0.1603(6)	0.9785(4)	9.3(3)
C(43)	0.4500(5)	0.0626(4)	0.9116(2)	5.1(2)
C(44)	0.3498(6)	0.1719(5)	0.8740(3)	7.1(2)
C(45)	0.2714(6)	0.1189(6)	0.8612(4)	8.2(3)
C(46)	0.2803(6)	0.0354(6)	0.8740(3)	7.5(2)
C(47)	0.3722(6)	0.0077(4)	0.8993(3)	6.2(2)
C(48)	0.1961(7)	-0.0241(6)	0.8623(5)	11.3(3)
C(49)	0.9485	-0.0082	0.5106	14.7(4)
C(50)	0.8647	-0.0446	0.4709	24.8(8)
C(51)	0.8623	0.0303	0.5909	29.1(9)
C(52)	0.7861	-0.0060	0.5605	29.3(9)
C(53)	0.7713	-0.0483	0.4986	22.7(7)
C(54)	0.6953	-0.0807	0.4557	20.3(6)

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

by the same intermolecular hydrogen bonds of Hbim$^-$ ligands; N(4)-N(18): 2.74Å; N(2)-N(16): 2.78 Å. The one-dimensional crinkled ribbon structure of complex **1** is more distorted by the formation of a ΔΔ ΛΛ sequence, compared with one-dimensional zigzag chain structures built up by a ΛΛ ΔΛ sequence with alternate arrangements of Δ and Λ optical isomers[7]. The one-dimensional chain distortion of the building block **1** has the space which can include free ligands of a 4,4'-dimethyl-2,2'-dipyridine in the crystal structure. However, the zigzag chain structure built up by alternate arrangements of a ΔΛ ΔΛ sequence has no space including the large organic molecule such as free ligands because of the high density packing of zigzag ribbon structures.

Results

An additional goal was to define the generality of ΔΛ ΔΛ zigzag ribbon formations for a kind of substituents on bidentate chelate ligand L, other than two $Hbim^-$ ligands, in a building block *cis*-$[Ni(Hbim)_2(L)]$. However, our immediate interest was to define structures and sequences of a series of molecular crystals differing only in substitution at one position. We found another ΔΔ ΛΛ sequence of arrangements of Δ and Λ optical isomers of the building block 1 to form crinkled-ribbon format. It is believed that this set of structures might serve as a systematic understanding of the relation of molecular to crystal structure.

ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture, Japan. The authors thank the Analytical Center, Osaka City University, for the use of a 4-Circle Single Crystal X-ray Diffractometer (Rigaku AFC-5R).

REFERENCES

1. J. A. Zerkowski, J. C. MacDonald, C. T. Seto, D. A. Wierda and G. M. Whitesides, J. Am. Chem. Soc., 116, 2382 (1994)
2. G. R. Desiraju, Crystal Engineering: The Design of Organic Solids (Elsevier: New York, 1989).
3. M. C. Etter, Acc. Chem. Res., 23, 120 (1990).
4. M. Tadokoro, K. Isobe and K. Nakasuji, Mol. Crst. Liq. Cryst.., in press (1996)
5. P. T. Beurskens, G. Admiraal, G. Beurskens, W. p. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smykalla, C. PATTY, 1992. Structure Analysis Programs with Intelligent Control (Rigaku Crop., Tokyo, Japan, 1991).
6. teXsan. Crystal Structure Analysis Package. Molecular Structure Crop. (the Woodlands, TX, 1985 and 1992).
7. M. Tadokoro, K. Isobe and K. Nakasuji, Mol. Cryst. Liq. Cryst., 278, 213 (1996).