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

Preparation of Nanoporous Molecular Based-Solid Produced by Tris-2,2′-Biimidazolate Co^{III} Complexes

Makoto Tadokoro [a], Takumasa Shiomi [a], Tomoko Shiromizu [a], Kiyoshi Isobo [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, Takumasa Shiomi, Tomoko Shiromizu, Kiyoshi Isobo, Keiji Matsumoto & Kazuhiro Nakasuji (1997): Preparation of Nanoporous Molecular Based-Solid Produced by Tris-2,2′-Biimidazolate Co^{III} Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 235-239

To link to this article: http://dx.doi.org/10.1080/10587259708044571

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 235–239
Reprints available directly from the publisher
Photocopying permitted by license only

PREPARATION OF NANOPOROUS MOLECULAR BASED-SOLID PRODUCED BY TRIS-2,2'-BIIMIDAZOLATE Co^{III} COMPLEXES

MAKOTO TADOKORO[1], TAKUMASA SHIOMI[1], TOMOKO SHIROMIZU[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 $[Co^{III}(Hbim)_3]$ (**1**) (Hbim = 2,2'-biimidazolate monoanion) is synthesized and its crystal structure is characterized by X-ray crystal analysis. (Crystal data: monoclinic, $C2/m$ (No. 12), $FW = 970.71$, $a = 17.144(5)$ Å, $b = 30.341(6)$ Å, $c = 16.422(5)$ Å, $\beta = 104.38(2)°$, $V = 8274(3)$ Å^3, $Z = 8$)
The crystal structure comprises assemblies of two-dimensional honeycomb sheet structures built up by alternate arrangements of Δ and Λ binary optical isomers of the building block **1**. The two-dimensional sheets are formed by complementary intermolecular hydrogen bonds of $Hbim^-$ ligands containing the building block **1**. Interestingly, two-dimensional sheets is stacked along c axis to form the microporous crystal with large channels.

INTRODUCTION

Research on microporous solids has focused largely on inorganic materials such as zeolites, pillared clays and other layered materials. Extended arrays based on networks such as AlB_2 and $ThSi_2$ have evoked wide attention[1-3]. Particular networks in this family are predicted to have unusual mechanical, thermal and electrical properties, especially when they contain large open features. Although syntheses of fragments of these prototypes have been achieved, extensions to three-dimensional networks by conventional synthesis have been difficult to realize. One approach to rational design of such networks with these fragments has been achieved by using the coordinating properties, the geometry, and the composition of transition metal complexes which are naturally predisposed to form a certain array of several well categorized solid ones. A goal of this reseach has been the design of new materials with specific properties such as selective adsorption and catalytic activity.[4,5] The tools of molecular synthesis of coordination compounds would be useful to engineer new types of microporous solids

constructed by transition metal ions. Here we report the design based on a modular approach and the crystal structure of an organic solid of a building block $[Co^{III}(Hbim)_3]$ (**1**) (Hbim = 2,2'-biimidazolate monoanion) with extended channels (diameter about 18 Å). Extended channels result from the stacking of the layers along the *c* axis. These layers are built up by the alternate arrangement of enantiomers of the Δ and Λ types, and these channels are filled with solvent molecules of methanol or ethyl acetate.

EXPERIMENTAL

Crystal Structure

The crystal data of [Co(Hbim)3] (**1**) are as follows: formula, $C_{36}H_{30}Co_2N_{24}O$, *monoclinic*, space group *C*2/m (No.12), ρ_{calc} = 1.558 g/cm^{-1}, Mo-Kα radiation, λ = 0.71069 Å, 6.0 < 2θ < 50°, 5981 reflections were collected, of which 2080 unique reflections ($I_O > 3\sigma(I_O)$) were used for refinement (294 parameters), converging to R = 0.129 and R_w = 0.190. The structure of complex **1** was solved by heavy-atom Patterson methods[6] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed in calculation. All calculations were performed using the teXsan[7] crystallographic software package. The final atomic coordinates of compound **1** are given in Table 2. All solvent molecules in the channel can not be calculated because of severely disorder of these molecules.

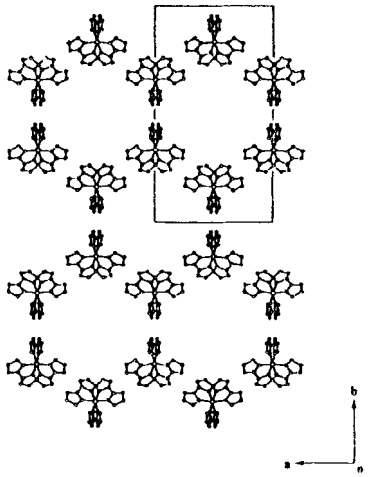

FIGURE 1 2D honeycomb sheet structure built up by alternate arrangements of Δ and Λ optical isomers of the building block **1** along the *c* axis.

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

		Distances	
Co(1) - N(1)	1.92(1)	Co(1) - N(1)	1.92(1)
Co(1) - N(3)	1.93(1)	Co(1) - N(3)	1.93(1)
Co(1) - N(6)	1.96(1)	Co(1) - N(6)	1.96(1)
Co(2) - N(7)	1.92(1)	Co(2) - N(7)	1.92(1)
Co(2) - N(9)	1.92(1)	Co(2) - N(9)	1.92(1)
Co(2) - N(11)	1.92(1)	Co(2) - N(11)	1.92(1)
		Angles	
N(1) - Co(1) - N(1)	90.7(7)	N(1) - Co(1) - N(3)	82.5(5)
N(1) - Co(1) - N(3)	93.9(5)	N(1) - Co(1) - N(6)	94.5(5)
N(1) - Co(1) - N(6)	171.7(5)	N(1) - Co(1) - N(3)	93.9(5)
N(1) - Co(1) - N(3)	82.5(5)	N(1) - Co(1) - N(6)	171.7(5)
N(1) - Co(1) - N(6)	94.5(5)	N(3) - Co(1) - N(3)	174.9(8)
N(3) - Co(1) - N(6)	93.2(5)	N(3) - Co(1) - N(6)	90.6(5)
N(3) - Co(1) - N(6)	90.6(5)	N(3) - Co(1) - N(6)	93.2(5)
N(6) - Co(1) - N(6)	81.1(7)	N(7) - Co(2) - N(7)	174.1(8)
N(7) - Co(2) - N(9)	81.1(6)	N(7) - Co(2) - N(9)	94.8(6)
N(7) - Co(2) - N(11)	91.2(6)	N(7) - Co(2) - N(11)	93.2(6)
N(7) - Co(2) - N(9)	94.8(6)	N(7) - Co(2) - N(9)	81.1(6)
N(7) - Co(2) - N(11)	93.2(6)	N(7) - Co(2) - N(11)	91.2(6)
N(9) - Co(2) - N(9)	92.4(9)	N(9) - Co(2) - N(11)	91.9(6)
N(9) - Co(2) - N(11)	173.1(6)	N(9) - Co(2) - N(11)	173.1(6)
N(9) - Co(2) - N(11)	91.9(6)	N(11) - Co(2) - N(11)	84.2(9)

[a] Estimated standard deviations are given in parentheses.

RESULTS AND DISCUSSION

Crystal Structure of complex **1**

A crystal of complex **1** suitable for X-ray analysis was obtained by recrystallization from a mixture of ethyl acetate-MeOH. An ORTEP view of complex **1** is shown in Figure 2 with the numbering scheme of non-hydrogen atoms. The selected bond distances and angles of complex **1** is given in Table 1. The crystal of complex **1** consists of trisbiimidazolate mononuclear Co(III) complexes ([Co(Hbim)3]), and some ethyl acetate and methanol molecules. Some ethyl acetate and methanol molecules are free from the coordination to the cobalt ion and would be captured in the crystal space with large hexagonal cavities produced by six [Co(Hbim)3] building blocks. These solvent molecules in cavities can not be determined because of the large thermal vibration and disorder.

The complex of [Co(Hbim)3] (**1**) contains the Co(III) atom coordinated by three bidentate $Hbim^-$ ligands through the lone pairs of the imine nitrogen atoms of the

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

atom	x	y	z	B_{eq}
Co(1)	0.0000	0.3353(1)	0.0000	4.45(7)
Co(2)	0.0000	0.3349(1)	0.5000	5.82(9)
N(1)	0.0350(8)	0.2909(4)	-0.0662(7)	4.8(3)
N(2)	0.1300(8)	0.2466(4)	-0.0854(8)	5.5(3)
N(3)	0.1107(7)	0.3325(4)	0.0634(7)	4.9(3)
N(4)	0.2315(7)	0.3011(5)	0.0781(8)	5.5(4)
N(5)	0.035(1)	0.4426(8)	-0.140(2)	18.3(9)
N(6)	0.0201(8)	0.3843(4)	-0.0695(8)	4.9(3)
N(7)	0.0790(8)	0.3316(4)	0.4353(9)	5.6(4)
N(8)	0.1899(10)	0.2961(5)	0.4150(10)	8.0(5)
N(9)	0.0696(10)	0.2911(5)	0.5650(9)	6.9(4)
N(10)	0.180(1)	0.2505(6)	0.590(1)	9.7(5)
N(11)	0.0579(9)	0.3818(4)	0.5671(9)	5.9(4)
N(12)	0.0716(9)	0.4554(5)	0.5871(8)	6.2(4)
C(1)	0.158(1)	0.3545(6)	0.129(1)	6.1(5)
C(2)	0.236(1)	0.3332(6)	0.142(1)	6.6(5)
C(3)	0.000(1)	0.2644(6)	-0.135(1)	5.7(5)
C(4)	0.061(1)	0.2365(5)	-0.145(1)	5.7(4)
C(5)	0.1129(9)	0.2780(5)	-0.0374(9)	4.4(4)
C(6)	0.1548(9)	0.3019(5)	0.0353(9)	4.4(4)
C(7)	0.041(1)	0.3918(9)	-0.146(1)	7.8(6)
C(8)	0.026(1)	0.4569(10)	-0.085(1)	8.1(7)
C(9)	0.0111(9)	0.4239(5)	-0.0366(9)	4.5(4)
C(10)	0.158(1)	0.3281(7)	0.354(1)	7.9(6)
C(11)	0.089(1)	0.3502(7)	0.359(1)	7.0(5)
C(12)	0.136(1)	0.3025(6)	0.465(1)	6.7(5)
C(13)	0.1318(10)	0.2794(7)	0.534(1)	6.3(5)
C(14)	0.149(2)	0.2449(8)	0.658(1)	10.8(8)
C(15)	0.074(2)	0.2698(7)	0.642(2)	10.2(8)
C(16)	0.118(1)	0.3857(6)	0.639(1)	6.3(5)
C(17)	0.127(1)	0.4308(7)	0.651(1)	6.6(5)
C(18)	0.034(1)	0.4199(7)	0.539(1)	6.5(5)

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

imidazole rings. The Co-N lengths of $[Co(Hbim)_3]^-$ have similar distances ot one another and fall in the range of 1.92(1) - 1.96(1) Å. The coordination geometry is a distorted octahedron. The distortion is mainly resulted from small N-Co-N bite angles (the range of 81° to 84°) which are lager than N-Ni-N bite angles (the range of 78° to 79° of $[Ni(Hbim)_3]^-$ complexes).[8] This comes from the difference in the distances between nitrogens of $Hbim^-$ ligands and a metal ion, because the distortion of the 2,2'-biimidazolate ligand in complex **1** is similar to that in $[Ni(Hbim)_3]^-$.

The most important interaction found in the crystal structure of [Co(Hbim)3] (**1**) is intermolecular hydrogen bondings to form the microporous crystals along the *c* axis produced by stacking of the 2D-honeycomb sheet structures. The 2D-honeycomb sheet structures are built up by the complementary hydrogen bonding of NH-N type of the building block between the alternate arrangement of Δ and Λ optical isomers of each three building blocks of [Co(Hbim)3] (**1**) in the alternate arrangement: N(2)-N(4)*: 2.76(1) Å; N(5)-N(5)*: 2.62(4) Å.; N(8)*-N(10): 2.66(2) Å; N(12)-N(12)*: 2.70(1) Å. The 2D-honeycomb sheets stack along the *c* axis to create the channel structures with the diameter of the cavity of about 17 Å. The layers between 2D-sheets are separated by about ~4.0 Å (the mean value of the shortest interlayer C-C distances). Such channel structure is kept intact even if MeOH and ethyl acetate molecules in the crystal lattice are removed.

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. R. H. Baughman and D. S. Galvao, Nature, 365, 735 (1993)
2. R. Rubin and F. Diederich, Angew. Chem. int. Ed. Engl, 31, 1101 (1992)
3. C. Zheng and R. Hoffmann, Inorg. Chem., 28, 1074 (1989)
4. M. H. Powell and B. D. P. Wetters, Chem. Ind., 256 (1955)
5. R. M. Barrer, In Inclusion Compounds, J. L. Atwood J. E. D. Davies and D. D. MacNicol, Eds. (Academic Press: London, 1984) Vol.1 p191.
6. 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).
7. teXsan. Crystal Structure Analysis Package. Molecular Structure Crop. (the Woodlands, TX, 1985 and 1992).
8. M. Tadokoro, K. Isobe and K. Nakasuji, Mol. Crst. Liq. Cryst., in press (1996)