Construction of Supramolecular Complexes by Use of Planar Bis(β-diketonato)cobalt(II) Complexes as Building Blocks

Jun Yoshida,[1] Shin-ichi Nishikiori,*[1] and Reiko Kuroda[2,3]
[1]*Depatrment of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo,*
3-8-1 Komaba, Meguro-ku, Tokyo 153-8902
[2]*Department of Life Sciences, Graduate School of Arts and Sciences, The University of Tokyo,*
3-8-1 Komaba, Meguro-ku, Tokyo 153-8902
[3]*JST ERATO-SORST Kuroda Chiromorphology Team,*
4-7-6 Komaba, Meguro-ku, Tokyo 153-0041

(Received February 20, 2007; CL-070194; E-mail: cnskor@mail.ecc.u-tokyo.ac.jp)

As building blocks for the construction of supramolecular complexes, two bis(β-diketonato) Co^{II} complexes were examined. From the self assembly of each Co^{II} complex and a polypyridyl ligand, 2′,4′,6′-tri(4-pyridyl)pyridine, two types of polymer structures, 1D zigzag chain and 2D hexagonal net, were obtained.

Many types of supramolecular complexes have been constructed by the self-assembly of metal ions and ligands.[1] Although this method is useful and applicable to various combinations of metal ions and ligands, the resultant structures are often beyond our expectation. A reason is that metal ions can have several coordination modes. In order to construct the supramolecular structures as we design, we need to control the coordination mode and chemical reactivity of the metal ions. It is difficult to present measures applicable to all coordination forms. However, for the linear coordination form, the use of planar bis(β-diketonato) complexes is a promising way. Planar bis(β-diketo nato) complexes can accept additional ligands at the axial sites keeping their planar structures.[2] Therefore, bis(β-diketonato) complexes could be used as linear building blocks in the construction of supramolecular complexes. Moreover, bis(β-diketonato) complexes have other merits. Many derivatives of β-diketonato ligands are known and their syntheses are relatively easy.[2] Choosing an appropriate β-diketonato ligand makes it possible to adjust the chemical reactivity at the metal center. Bis (β-diketonato) complexes have no electric charge, and the resultant supramolecular complex comprised of a bis (β-diketonato) complex and a neutral ligand includes no counter ions. The existence of such counter ions usually makes it difficult to predict the resultant structures, especially in the solid state.

In spite of these merits, the use of bis (β-diketonato) complexes as building blocks in the construction of coordination polymers have not been investigated well.[3] In this study, to confirm the possibility and usefulness of bis (β-diketonato) complexes as building blocks we have examined two cases: one is the combination of a [Co^{II}(acac)$_2$(H$_2$O)$_2$] complex[4] (acac = pentane-2,4-dionato) and a polypyridyl ligand, 2′,4′,6′-tri(4-pyridyl)pyridine[5] (**L**); another is that of a [Co^{II}(acacCN)$_2$(H$_2$O)$_2$] complex[6] (acacCN = 3-cyano-pentane-2,4-dionato) and **L** (Chart 1). Single crystal X-ray diffraction analyses of two coordination polymers obtained from the above combinations were carried out.

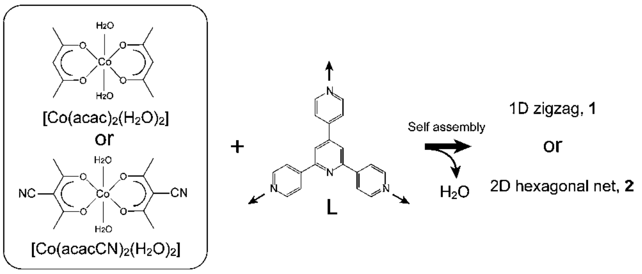

Chart 1.

Single crystals of [Co(acac)$_2$](**L**)(CHCl$_3$) (**1**) were obtained from a methanol–chloroform mixed solution containing [Co(acac)$_2$(H$_2$O)$_2$] and **L** after slow evaporation of the solvent at ambient temperature over a few hours.[7,12] Figure 1 shows a 1D zigzag structure found in **1**. The 1D zigzag chain is formed with the alternate linkage of [Co(acac)$_2$] and **L**, where [Co(acac)$_2$] and **L** work as a linear building block and a bidentate ligand, respectively. The noncoordinating pyridine moiety of **L** points to the H atom of a chloroform molecule, which is placed between adjoining 1D zigzag chains. As a ligand whose coordination ability is identical to **L**, 1,3,5-tri(4-pyridyl)-2,4,6-triazine (tpt) is well known and used. Many supramolecular structures of tpt complexes have been reported.[8] However, there are few examples of 1D zigzag structure as found in **1**.[9]

Single crystals of [Co(acacCN)$_2$]$_3$(**L**)$_2$(MeOH)$_4$ (**2**) were obtained from a methanol–chloroform mixed solution containing [Co(acacCN)$_2$(H$_2$O)$_2$] and **L** by the same procedure used in the preparation of **1**.[10,12] Figure 2 shows a 2D (6,3) type[11] hexagonal network found in **2**. The 2D hexagonal network is formed with the alternate linkage of [Co(acacCN)$_2$] and **L**, where [Co(acacCN)$_2$] and **L** work as a linear building block and a tridentate ligand, respectively. Through the large hexagonal windows, three equivalent 2D hexagonal networks are

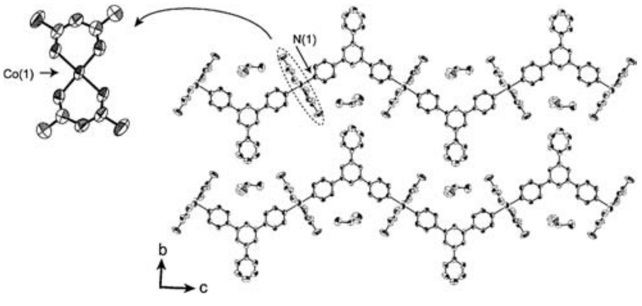

Figure 1. 1D zigzag structure of **1**.

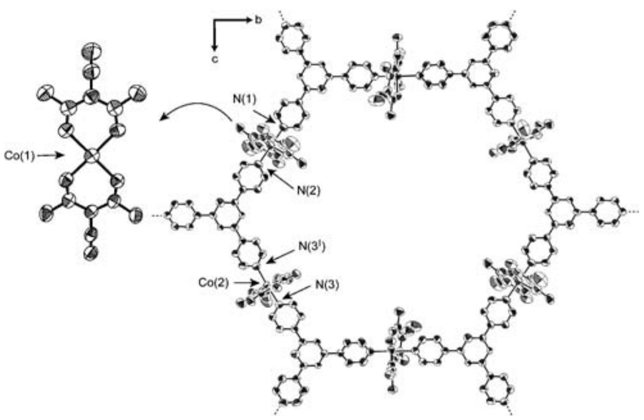

Figure 2. 2D (6,3) hexagonal network of **2** (symmetry code; I: $1 - x$, $1 - y$, $-z$).

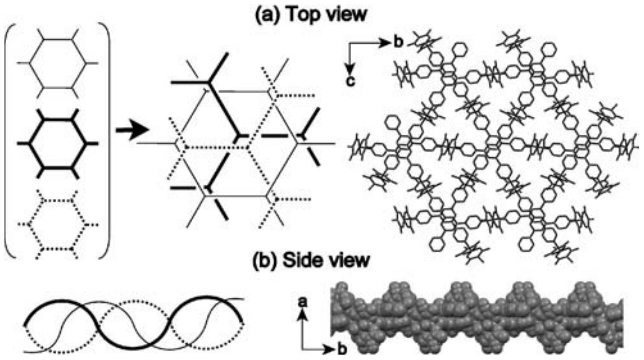

Figure 3. Triply interpenetrated 2D sheets in **2**. (a) Top view of schematic model (left) and stick model (right). (b) Side view of schematic model (left) and space-filling model (right).

woven into a three fold interpenetrated structure as shown in Figure 3. To our knowledge, this is the first example of three-fold interpenetration of the hexagonal networks constructed with **L** or tpt.

In **1** and **2**, [Co(acac)$_2$] and [Co(acacCN)$_2$] worked as linear building blocks keeping their planar structure, whereas **L** showed different coordinating behavior. The evident difference between **1** and **2** is the presence or absence of the cyano group introduced to the acac moiety. In our investigation on both crystal structures, we were not able to find any clear indication that the cyano group generates the different coordinating behavior of **L** in terms of steric effects or interactions with other components. The difference is considered to be originated in the difference of chemical reactivity or Lewis acidity of the bis (β-diketonato) complex moieties. The cyano groups of [Co(acacCN)$_2$] bring more Lewis acidity to the metal center by its electron-withdrawing function. The data of the bond length between Co and N of **L** support this effect: Co(1)–N(1) in **1** was 2.215(2) Å, while Co(1)–N(1), Co(1)–N(2), and Co(2)–N(3) in **2** were 2.144(2), 2.123(2), and 2.155(2) Å, respectively. It is probable that the difference of the affinity for **L** between the two bis (β-diketonato) complex moieties generates the structural difference between the two resultant coordination polymers. This finding suggests a possibility of the structural modification of coordination polymers through tuning Lewis acidity of the [Co(β-diketonato)$_2$] building block.

In summary, using two [Co(β-diketonato)$_2$] planar complexes as linear building blocks, two new supramolecular structures, 1D zigzag chain (**1**) and 2D hexagonal network (**2**), were constructed with the common ligand **L**. The structural difference found between **1** and **2** is considered to arise from the difference in Lewis acidity of Co^{II} in the [Co(β-diketonato)$_2$] building blocks, which was tunable by choosing the β-diketonato ligand.

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References and Notes

1 a) S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739. b) S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276.

2 a) D. P. Graddon, E. C. Watton, *J. Inorg. Nucl. Chem.* **1961**, *21*, 49. b) D. P. Graddon, *Coord. Chem. Rev.* **1969**, *4*, 1.

3 a) B.-Q. Ma, S. Gao, T. Yi, G.-X. Xu, *Polyhedron* **2001**, *20*, 1255. b) D. V. Soldatov, I. L. Moudrakovski, C. I. Ratcliffe, R. Dutrisac, J. A. Ripmeester, *Chem. Mater.* **2003**, *15*, 4810.

4 F. A. Cotton, R. C. Elder, *Inorg. Chem.* **1966**, *5*, 423.

5 J. Wang, G. S. Hanan, *Synlett* **2005**, *8*, 1251.

6 a) O. Angelova, J. Macicek, M. Atanasov, G. Petrov, *Inorg. Chem.* **1991**, *30*, 1943. b) C. M. Silvernail, G. Yap, R. D. Sommer, A. L. Rheingold, V. W. Day, J. A. Belot, *Polyhedron* **2001**, *20*, 3113.

7 Crystal data for **1**. $C_{31}H_{29}N_4O_4Cl_3Co$, $M_r = 686.86$, monoclinic, space group $I2/a$ (#15), $a = 9.352(5)$, $b = 15.145(5)$, $c = 26.961(5)$ Å^3, $\beta = 54.240(5)^\circ$, $V = 3099(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.47\,g\,cm^{-1}$, $\mu(Mo\,K\alpha) = 0.855\,mm^{-1}$. 5348 unique reflections. Final residuals were $R_1 = 0.055$, $wR2 = 0.138$ and GOF = 0.828 for 256 parameters and 2062 reflections ($I_{net} > 2\sigma(I_{net})$). CCDC-640931.

8 a) S. R. Batten, B. F. Hoskins, R. Robson, *J. Am. Chem. Soc.* **1995**, *117*, 5385. b) S. R. Batten, B. F. Hoskins, B. Moubaraki, K. S. Murray, R. Robson, *Chem. Commun.* **2000**, 1095. c) C. S. A. Fraser, M. C. Jennings, R. J. Puddephatt, *Chem. Commun.* **2001**, 1310. d) K. Biradha, M. Fujita, *Angew. Chem., Int. Ed.* **2002**, *41*, 3392. e) B.-Q. Ma, P. Coppens, *Chem. Commun.* **2003**, 2290.

9 a) D. E. Hagrman, J. Zubieta, *J. Solid State Chem.* **2000**, *152*, 141. b) R. S. Rarig, Jr., J. Zubieta, *J. Chem. Soc., Dalton Trans.* **2001**, 3446. c) F. A. Cotton, C. Lin, C. A. Murillo, *J. Chem. Soc., Dalton Trans.* **2001**, 499. d) J. P. H. Charmant, A. H. M. Monowar Jahan, N. C. Norman, A. Guy Orpen, T. J. Podesta, *CrystEngComm* **2004**, *6*, 29.

10 Crystal data for **2**. $C_{80}H_{86}N_{14}O_{16}Co_3$, $M_r = 1676.4$, monoclinic, space group $P2_1/c$ (#14), $a = 10.4230(3)$, $b = 15.4308(5)$, $c = 26.7556(9)$ Å, $\beta = 77.2110(10)^\circ$, $V = 4196.49(10)$ Å^3, $Z = 2$, $D_{calcd} = 1.33\,g\,cm^{-1}$, $\mu(Mo\,K\alpha) = 0.658\,mm^{-1}$. 14738 unique reflections. Final residuals were $R_1 = 0.056$, $wR2 = 0.115$ and GOF = 0.741 for 528 parameters and 3857 reflections ($I_{net} > 2\sigma(I_{net})$). CCDC-640932.

11 A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, **1984**, Chap. 3.

12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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