Solvent-dependent Assembly of Discrete and Continuous CoCl_2 Adamantane-based Ligand Complexes: Observations by CSI-Mass Spectrometry and X-ray Crystallography

Kazuaki OHARA,[†] Masahide TOMINAGA, Isao AZUMAYA, and Kentaro YAMAGUCHI[†]

Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, Shido, Sanuki, Kagawa 769-2193, Japan

Discrete and continuous coordination structures were obtained in single crystals of CoCl_2 and an adamantane-based bidentate ligand bearing imidazolyl groups, depending on the methanol concentration in a methanol-chloroform mixture. Single-crystal X-ray structure analysis revealed that the metal centers exhibited a tetrahedral geometry in the discrete complex and an octahedral geometry in the continuous metal complex. Conventional analytical methods, including UV-vis and NMR spectroscopy, could not identify those two complexes in solution. In contrast, cold-spray ionization mass spectrometry could detect differences between the discrete complex and the continuous metal complex, and ion peaks due to continuous ligand adducts were found only in the spectrum of the continuous metal complex.

Keywords Coordination bonding, cold-spray ionization mass spectrometry, solvent-dependent, single-crystal X-ray analysis

(Received June 25, 2013; Accepted July 9, 2013; Published August 10, 2013)

Significant attention has recently been given to coordination chemistry, which has found applications in the construction of complicated or nano-sized structures, catenanes,^{1,2} rotaxanes,³⁻⁵ helices,^{6,7} molecular squares,⁸⁻¹⁰ tetrahedral hosts,¹¹⁻¹⁶ and so on.¹⁷⁻²¹ Coordination compounds exist not only as discrete molecules in solution, but also as compounds with infinite periodicity in the crystal state. Coordination polymers (CPs) and metal-organic frameworks (MOFs) are well-known crystals constructed by an organic compound and a metal. Porous CPs (PCPs) and MOFs, in particular, are highly potential materials for gas storage,²²⁻²⁴ ion exchange,²⁵⁻²⁸ heterogeneous catalysis,²⁹⁻³¹ separation,^{29,32-36} and non-linear optics,³⁷⁻³⁹ because of the nano-space separated from bulk space.

Structure construction with a coordination bond plays a critical role in the formation of a complicated structure and the introduction of functionality into the structure for basic research and industrial applications. In structure control, it is important to adjust the metal-ligand stoichiometry based on the number of coordination sites or the coordination environment. For example, Lehn and coworkers⁴⁰ demonstrated the spontaneous formation of a cylindrical complex from five ligands and six metal ions, in which two hexaazatriphenylene derivatives acting as the planar molecule and three bisbipyridyl ligands linked at the 5,5' positions acting as the pillar molecule were connected by three copper ions. The structure was characterized by ¹H NMR spectroscopy, fast atom bombardment mass spectrometry (MS), and single-crystal X-ray structure analysis. The concept of adjusting metal-ligand stoichiometry has been

widely accepted in discrete complexes and CPs, depending on the metal coordination geometry and the ligand binding site. However, complex preparation relies on many factors, such as the temperature, concentration, and the counter ion. For instance, Fujita and coworkers⁴¹ demonstrated the treatment of $\text{Pd}(\text{NO}_3)_2$ and a ditopic bidentate ligand assembled into a mixture of M_4L_8 and M_3L_6 box-like structures, depending on the ratio of dimethylsulfoxide to acetonitrile. In such an environment-dependent complex formation, advanced functions, including molecular switching and molecular catch and release, for instance, have been obtained in recent years. However, structure elucidation of obtained complexes is generally difficult by using only ¹H NMR analysis in the case that the numbers of ligands and metals are not known. Therefore, limited studies of environment-dependent complexes have been reported up to the present.⁴²⁻⁴⁶

Conventional MS using electron ionization, chemical ionization, fast atom bombardment, and electro-spray ionization cannot detect large coordination complexes because the weak coordination bonds dissociate during ionization. Cold-spray ionization MS (CSI-MS) is one of the most promising solutions to this problem,⁴⁷ as it can detect coordination complexes without dissociation to give the numbers of ligands and metals as well as ions based on the solvent adducts. In our previous work,⁴⁸ we clearly observed oligomeric coordination species of CP in the crystallization solution by CSI-MS. We believe that CSI-MS is suitable for the detection of a complex constructed by a weak non-covalent bond, namely, a coordination bond, because it has a large dynamic range and high sensitivity even if the complex has very low solubility. In this work, we demonstrated the construction of two crystal structures: a discrete cyclic complex with tetrahedral geometry and a

[†] To whom correspondence should be addressed.

E-mail: kyamaguchi@kph.bunri-u.ac.jp (K. Y.); kohara@kph.bunri-u.ac.jp (K. O.)

polymeric 1D complex bearing cyclic units with octahedral geometry, depending on the methanol concentration in a methanol-chloroform mixture, using the same ligand as that used in metal-ligand stoichiometry (Scheme 1). The crystallization solution was investigated by CSI-MS, UV-vis, and NMR spectroscopy in order to discuss how solvent differences affect the formation of a discrete complex and a continuous metal complex.

The continuous metal complex obtained in the present study was formed from a bidentate organic ligand with two imidazolyl groups connected to a rigid 1,3-diphenyladamantane spacer, which is intrinsically capable of forming a bridge or a ring with metals. Owing to its nature, ligand **1** (L) can form diverse supramolecular architectures in crystals. The ligand was prepared from a copper(I)-catalyzed reaction between imidazole and 1,3-bis(4-iodophenyl)adamantane with a yield of 50%. In a methanol-chloroform mixture (1:4 and 1:2), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and L at 1:1 ratio were stirred for 5 min. After vapor diffusion of tetrahydrofuran into the solution for 1 day at room temperature, blue (crystal **1a**) and colorless (crystal **1b**) crystals were obtained from 1:4 and 1:2 MeOH/ CHCl_3 , respectively.

Single-crystal X-ray structure analysis (see Supporting Information) revealed two different crystal structures, as shown in Figs. 1 and 2. In crystal **1a**, triclinic $P\bar{1}$, the tetrahedral cobalt atoms coordinated to two Cl atoms and two nitrogen atoms of the imidazolyl groups (Co-N, 2.010(6) and 2.023(5) Å; Co-Cl, 2.247(2) and 2.238(2) Å) to form a complex of

$(\text{CoCl}_2)_2\text{L}_2$ (Fig. 1a), exhibiting a discrete cyclic shape bearing a 11.0×17.1 Å rhombic cavity (Fig. 1b). The cavity was filled with disordered chloroform molecules at 50% occupancy in each of the two independent positions. Packing analysis revealed that the stacking of a quasi-planar 2D layer with a CH-halogen interaction gave a 3D network structure (See Supporting Information for details). In crystal **1b**, monoclinic $C2/c$, the octahedral cobalt atoms coordinated to two Cl atoms in *trans* and four nitrogen atoms of the imidazolyl groups (Co-N, 2.113(3) and 2.130(3) Å; Co-Cl, 2.5811(9) Å) (Figs. 2a and 2b). The bidentate L bridging the two adjacent cobalt centers formed an infinite 1D polymer structure $[\text{CoCl}_2\text{L}_2]_n$ (Fig. 2c), where *n* is an integer, having a cyclic unit similar to that observed in the discrete complex of crystal **1a**. The cavity of one cyclic structure, $[\text{CoCl}_2\text{L}_2]_2$, was interpenetrated by another cyclic structure, $[\text{CoCl}_2\text{L}_2]_2$ (Fig. S4b, Supporting Information), thereby exhibiting a 3D network structure. In this structure, 1D channels extending parallel to the *c* axis were observed (Fig. 2d).

CSI-MS revealed two structures, discrete and continuous metal complexes, in solution. In the CSI-MS spectrum of the methanol-rich solution for crystallization containing the adamantane-based ligand and CoCl_2 , several molecular ion peaks were clearly observed from *m/z* 724.2 to 1986.9. Some of the ion peaks were assigned to chemically important coordination complexes without coordination bond dissociation. For example, the molecular ion peak at *m/z* 934.9 was ascribed to the $[\text{Co}_3\text{ClL}_3]$ complex with the solvent adduct in the doubly charged state. It should be emphasized that CSI-MS involves solvent adducts very often.⁴³ The assignment of observed ion peaks is summarized in Table 1. The difference in mass number between the adjacent peaks corresponds to the doubly charged adamantane-based ligand, as shown in Fig. 3b. A Co_3L_m complex can form a part of the 1D chain structure observed in crystal **1b**, ignoring the presence of the counteranion cobalt when the number of ligands, *m*, is from 2 to 8. All of the suggested complexes with one chloride and several solvent adducts were clearly observed by CSI-MS. However, a smaller or larger number of ligands could not form a part of the polymer structure, $[\text{CoCl}_2\text{L}_2]_n$. On the other hand, for ion peaks corresponding to low-molecular-weight complexes, the methanol-poor solution appeared in the CSI-MS spectrum in Fig. 3a. No ion peaks due to continuous ligand adducts were found in Fig. 3b, and a $[\text{Co}_3\text{ClL}_2]$ complex with several solvent adducts was observed in both methanol-rich and -poor solutions.

Scheme 1 Schematic representation of the solvent-dependent formation of a discrete cyclic complex and polymeric 1D complex bearing cyclic parts, depending on the methanol concentration in a chloroform solution.

Fig. 1 (a) ORTEP representation of crystal **1a** of an asymmetric unit. The thermal ellipsoids are drawn at 30% probability. (b) Cyclic structure $(\text{CoCl}_2)_2\text{L}_2$ as a space-filling model. One chloroform molecule occupies the inside of the cyclic $(\text{CoCl}_2)_2\text{L}_2$ complex at the inversion center. The disorder of the chloroform is not shown for clarity. Color codes: C (gray), N (blue), Cl (green), Co (magenta).

Fig. 2 ORTEP representation of crystal **1b**. (a) Independent molecules and (b) a discrete cyclic structure. The thermal ellipsoids are drawn at the 30% probability level. The disordered solvents, chloroform and methanol, are not shown for clarity. Color codes: C (gray), N (blue), Cl (green), Co (magenta). (c) Interpenetrated 2D layer composed of 1D polymers bearing cyclic parts. (d) Top view along *c* axis of 3D network structure. Two different 2D layers are intercrossed at the cavity. Disordered solvent molecules are omitted for clarity.

The observed peak lists and assignments are summarized in Table S1, Supporting Information. Under the condition for continuous metal complex formation, the coordination oligomers that corresponded to a part of CP were observed in solution. On the other hand, under the discrete complex formation condition, no continuous ligand adducts were observed in solution. In the ^1H NMR spectra, signals of the adamantane ligand under the discrete complex formation condition were shifted upfield relative to the signals before complexation. The same chemical shift changes were observed under the continuous metal complex formation condition (Fig. S5, Supporting Information). However, the chemical shift differences between those two different conditions did not yield any structure information. In the UV-vis spectra, the absorption bands from cobalt ion also gave no differences between those two conditions before and after crystallization, although the cobalt ion gave a different absorption spectrum, depending on its coordination environment (Fig. S6, Supporting Information). We believe that a continuous cobalt complex was kinetically produced by complexation so that the number of octahedral cobalt ions was very small in

Fig. 3 CSI-MS spectra of a crystallization solution after 1 day in positive ion mode. (a) Under conditions favoring the formation of the discrete complex, only the ion peaks corresponding to the ligand and small complex are observed. (b) Under conditions favoring the formation of the polymeric complex, several ion peaks are observed with the sequential addition of L.

Table 1 Observed and calculated mass numbers of Co and adamantane-based ligand, L complexes for filtrate of **1b** crystallization solution and their errors

Chemical formula with charged state	Observed mass (charged state)	Calculated mass	Error, ppm
$[\text{Co}_3\text{CIL}_2(\text{THF})_2(\text{H}_2\text{O})_{14}]^{2+}$	724.2452(+2)	724.2465	-1.8
$[\text{Co}_3\text{CIL}_3(\text{THF})_2(\text{H}_2\text{O})_{14}]^{2+}$	934.8587(+2)	934.8639	-5.5
$[\text{Co}_3\text{CIL}_4(\text{THF})_2(\text{H}_2\text{O})_{14}]^{2+}$	1145.4709(+2)	1145.4813	-7.9
$[\text{Co}_3\text{CIL}_5(\text{THF})_2(\text{H}_2\text{O})_{14}]^{2+}$	1355.5845(+2)	1355.5969	-8.9
$[\text{CoCIL}_3]^+$	1354.5822(+1)	1354.5956	-10.0
$[\text{Co}_3\text{CIL}_6(\text{THF})_2(\text{H}_2\text{O})_{14}]^{2+}$	1565.6929(+2)	1565.7127	-12.1
$[\text{Co}_3\text{CIL}_7(\text{THF})_2(\text{H}_2\text{O})_{14}]^{2+}$	1775.7931(+2)	1775.8284	-19.5
$[\text{Co}_3\text{CIL}_8(\text{THF})_2(\text{H}_2\text{O})_{14}]^{2+}$	1986.9137(+2)	1986.9474	-15.9

solution. Despite such subtle changes in solution, CSI-MS enabled discrimination between discrete coordination species and oligomeric coordination species in solution.

In summary, we empirically succeeded in the solvent-dependent assembly of a discrete cyclic complex and a continuous metal complex having cyclic units formed from adamantane-based bidentate ligands and cobalt ions of the same stoichiometry. The formation of the two complexes depended on the methanol concentration in the crystallization solution, which directed tetrahedral or octahedral cobalt hybridization. In the crystallization solution, CSI-MS could distinguish subtle changes between discrete and oligomeric structures, which could not be accomplished by other methods, such as UV-vis and NMR spectroscopy. We believe that CSI-MS is not only a powerful and efficient tool to find new structures for coordination complexation, depending on the environment condition, but also a promising analytical method for use in coordination chemistry.

Supporting Information

General experimental procedure, crystallographic data and structure, characterization of organic ligands, CSI-MS assignment, and UV-vis and ¹H NMR data are summarized. Crystal structure data of **1a** and **1b** have been deposited with the Cambridge Crystallographic Data Centre in the CIF format as CCDC-886044 and -886045. This material is available free of charge on the Web at <http://www.jsac.or.jp/analsci/>.

References

1. C. O. Dietrich-Buchecker, J.-P. Sauvage, and J. P. Kintzinger, *Tetrahedron Lett.*, **1983**, 24, 5095.
2. J.-P. Sauvage, *Acc. Chem. Res.*, **1990**, 23, 319.
3. H. Ogino, *J. Am. Chem. Soc.*, **1981**, 103, 1303.
4. R. S. Wylie and D. H. Macartney, *J. Am. Chem. Soc.*, **1992**, 114, 3136.
5. Y. Suzaki, T. Taira, and K. Osakada, *Dalton Trans.*, **2006**, 5345.
6. M. Ikeda, Y. Tanaka, T. Hasegawa, Y. Furusho, and E. Yashima, *J. Am. Chem. Soc.*, **2006**, 128, 6806.
7. H. Miyake and H. Tsukube, *Chem. Soc. Rev.*, **2012**, 41, 6977.
8. M. Fujita, J. Yazaki, and K. Ogura, *J. Am. Chem. Soc.*, **1990**, 112, 5645.
9. R. D. Sommer, A. L. Rheingold, A. J. Goshe, and B. Bosnich, *J. Am. Chem. Soc.*, **2001**, 123, 3940.
10. D. K. Chand, K. Biradha, M. Kawano, S. Sakamoto, K. Yamaguchi, and M. Fujita, *Chem. Asian J.*, **2006**, 1-2, 82.
11. C. Brückner, R. E. Powers, and K. N. Raymond, *Angew. Chem. Int. Ed.*, **1998**, 37, 1837.
12. M. Albrecht and R. Fröhlich, *Bull. Chem. Soc. Jpn.*, **2007**, 80, 797.
13. M. Albrecht, I. Janser, S. Meyer, P. Weis, and R. Fröhlich, *Chem. Commun.*, **2003**, 2854.
14. D. W. Johnson and K. N. Raymond, *Inorg. Chem.*, **2001**, 40, 5157.
15. D. L. Caulder, C. Brückner, R. E. Powers, S. König, T. N. Parac, J. A. Leary, and K. N. Raymond, *J. Am. Chem. Soc.*, **2001**, 123, 8923.
16. D. L. Caulder and K. N. Raymond, *J. Chem. Soc. Dalton Trans.*, **1999**, 1185.
17. M. Fujita, D. Oguro, M. Miyazawa, K. Yamaguchi, and K. Ogura, *Nature*, **1995**, 378, 469.
18. B. F. Abrahams, S. J. Egan, and R. Robson, *J. Am. Chem. Soc.*, **1999**, 121, 3535.
19. B. Olenyuk, M. D. Levin, J. A. Whiteford, J. E. Shield, and P. J. Stang, *J. Am. Chem. Soc.*, **1999**, 121, 10434.
20. M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe, and O. M. Yaghi, *J. Am. Chem. Soc.*, **2001**, 123, 4368.
21. R. M. McKinlay, G. W. V. Cave, and J. L. Atwood, *Proc. Natl. Acad. Sci. U. S. A.*, **2005**, 102, 5944.
22. H. Li, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi, *Nature*, **1999**, 402, 276.
23. U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt, and J. Pastré, *J. Mater. Chem.*, **2006**, 16, 626.
24. A. U. Czaja, N. Trukhan, and U. Müller, *Chem. Soc. Rev.*, **2009**, 38, 1284.
25. P. Wang, J.-P. Ma, Y.-B. Dong, and R.-Q. Huang, *J. Am. Chem. Soc.*, **2007**, 129, 10620.
26. F. Costantino, A. Donnadio, and M. Casciola, *Inorg. Chem.*, **2012**, 51, 6992.
27. M. Nagarathinam, A. Chanthapally, S. H. Lapidus, P. W. Stephens, and J. J. Vittal, *Chem. Commun.*, **2012**, 48, 2585.
28. X. Cui, A. N. Khlobystov, X. Chen, D. H. Marsh, A. J. Blake, W. Lewis, N. R. Champness, C. J. Roberts, and M. Schröder, *Chem. Eur. J.*, **2009**, 15, 8861.
29. J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, and K. Kim, *Nature*, **2000**, 404, 982.
30. C.-D. Wu, A. Hu, L. Zhang, and W. Lin, *J. Am. Chem. Soc.*, **2005**, 127, 8940.
31. L. Ma, C. Abney, and W. Lin, *Chem. Soc. Rev.*, **2009**, 38, 1248.
32. J.-R. Li, R. J. Kuppler, and H.-C. Zhou, *Chem. Soc. Rev.*, **2009**, 38, 1477.
33. B. Chen, C. Liang, J. Yang, D. S. Contreras, Y. L. Clancy, E. B. Lobkovsky, O. M. Yaghi, and S. Dai, *Angew. Chem., Int. Ed.*, **2006**, 45, 1390.
34. S. Shimomura, S. Horike, R. Matsuda, and S. Kitagawa, *J. Am. Chem. Soc.*, **2007**, 129, 10990.
35. L. Pan, D. H. Olson, L. R. Ciemnolonski, R. Heddy, and J. Li, *Angew. Chem., Int. Ed.*, **2006**, 45, 616.
36. L. Pan, B. Parker, X. Huang, D. H. Olson, J. Y. Lee, and J. Li, *J. Am. Chem. Soc.*, **2006**, 128, 4180.
37. C. Janiak, *Dalton Trans.*, **2003**, 2781.
38. W. Lin, Z. Wang, and L. Ma, *J. Am. Chem. Soc.*, **1999**, 121, 11249.
39. L. Wang, M. Yang, G. Li, Z. Shi, and S. Feng, *Inorg. Chem.*, **2006**, 45, 2474.
40. P. Baxter, J.-M. Lehn, A. DeCain, and J. Fischer, *Angew. Chem., Int. Ed.*, **1993**, 32, 69.
41. K. Suzuki, M. Kawano, and M. Fujita, *Angew. Chem., Int. Ed.*, **2007**, 46, 2819.
42. K. Biradha, Y. Hongo, and M. Fujita, *Angew. Chem., Int. Ed.*, **2002**, 41, 3395.
43. J. Aimi, Y. Nagamine, A. Tsuda, A. Muranaka, M. Uchiyama, and T. Aida, *Angew. Chem., Int. Ed.*, **2008**, 47, 5153.
44. D. Braga, L. Maini, P. P. Mazzeo, and B. Ventura, *Chem. Eur. J.*, **2010**, 16, 1553.
45. Z.-Z. Lu, R. Zhang, Y.-Z. Li, Z.-J. Guo, and H.-G. Zheng, *J. Am. Chem. Soc.*, **2011**, 133, 4172.
46. M. Chang, A. Kobayashi, K. Nakajima, H.-C. Chang, and M. Kato, *Inorg. Chem.*, **2011**, 50, 8308.
47. K. Yamaguchi, *J. Mass Spectrom.*, **2003**, 38, 473.
48. K. Ohara and K. Yamaguchi, *Anal. Sci.*, **2012**, 28, 635.