Concomitant crystallization of two polymorphs—a ring and a helix: concentration effect on supramolecular isomerism

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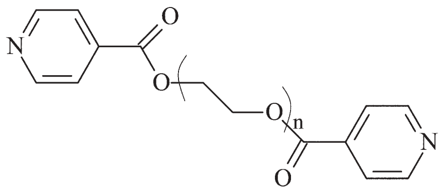
For the first time in Ag coordination chemistry, two supramolecular isomers, a ring and a helix, are isolated from the same mother liquor as a result of concentration effects.

During the past years, there has been considerable interest in the supramolecular architectures that can possibly be obtained by the combination of organic building blocks with transition metal ions.[1] In this context, it has been shown that coordination polymers constructed from rigid organic ligands show parallels with some standard inorganic compounds such as *i.e.* graphite, diamond or wurtzite.[2] However, with more flexible building blocks, the structures become less predictable.[3] When considering likely transition metal geometries, some predictions can be made, as to whether for instance a one- or two-dimensional compound is expected. But weaker supramolecular forces such as hydrogen bonding, π-interactions, or the coordination ability of the counter anions as well as the presence of solvent molecules are all able to strongly influence the final framework,[1,4] making polymorphism and pseudo-polymorphism more probable. Polymorphism is a phenomenon observed throughout all branches of chemistry as soon as a solid crystalline compound has the possibility to adopt at least two different arrangements in the solid state.[5] One example of polymorphism can be supramolecular isomerism in which the packing is insofar different, as for instance coordination polymers *versus* monomers can be obtained.[6] Different polymorphs may have very different physical and chemical properties, and are therefore interesting study objects. Supramolecular crystal engineering is a related attractive research field with the aim of exerting more control over the solid state structures.[7,8]

So far, our group has been interested in the design of predictable low-dimensional polymers containing alkaline earth metal ions.[9–12] With a view to oxide materials, we now aim at single source precursors containing all metal ions necessary for the desired product. In order to synthesize mixed metal compounds, a series of ligands derived from pyridine was designed, possessing two different coordination sites encoded for two types of metal ions (Scheme 1). We here report on two compounds obtained with the ligand L for $n = 2$ and $AgClO_4$. These two compounds are important because they are the first examples in silver coordination chemistry, yielding two polymorphs (a ring and a helix) as a function of concentration in the same reaction sample. It is reasonable to expect such phenomena in future studies owing to the weakness of the forces implied in the structure formation, both structures being apparently of similar energy.



Scheme 1 Ligand designed for accepting two different metal ions.

Single crystals of both compounds are obtained in an H-tube,† with an aqueous solution of silver salt on one side, a THF solution of ligand on the other side, both connected *via* a mixture of both solvents. Slow diffusion of the ligand into the metal salt solution and *vice versa* yields the ring-forming compound $[Ag(L)]ClO_4$, **1**, which was obtained on the side of the silver salt. **1** crystallizes in the triclinic space group $P\bar{1}$ (no. 2)[13] with half of a molecule per asymmetric unit. In a molecule, two metal ions are bridged by two ligands L to form an oval-shaped ring (Fig. 1a). The shortest contact across the loop is the Ag–Ag contact of 3.146(1) Å, the longest is between opposite hydrogen atoms in C_2H_4-groups at *ca.* 20 Å (Fig. 1b). Interestingly, the short Ag–Ag contact is not bridged by anions in a pincer fashion as observed in coordination polymers formed by pairs of one-dimensional chains where silver is

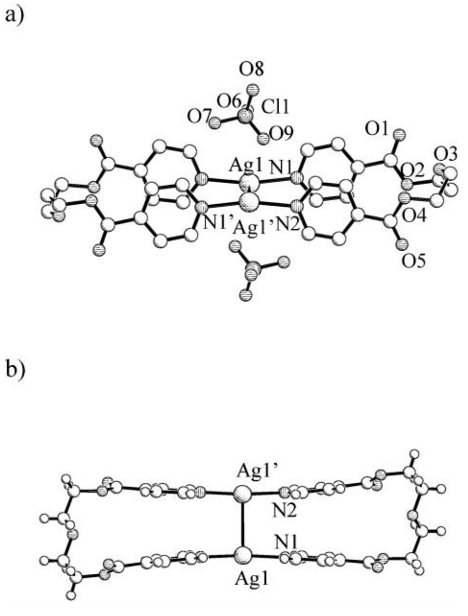


Fig. 1 a) View of the molecular structure of **1**, H-atoms omitted for clarity; b) top-view of **1**, showing Ag–Ag closest contacts; anions omitted for clarity (symmetry operation (′) $-x$, $-y$, $-z$).

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bridged by other anions such as NO_3^-.[14] Among the Ag–O contacts that can be considered as weak interactions between the cation and the perchlorate anion, the shortest is Ag1–O9 [2.931(1) Å]. The Ag1–N distances [2.150(6) (N1) and 2.155(6) Å (N2′)] are almost identical, and the angle N1–Ag1–N2′ [167.8(2)°] is far from linear due to the deformation resulting from Ag–Ag contacts. There is no obvious reason from solid state packing why the silver atoms should come that close to each other if it were not for metal–metal interactions. The rings are arranged in a parallel fashion with the empty space in between filled with the perchlorate anions. Some of the oxygen atoms of the latter are weakly bonded to the hydrogen atoms of the ligand L, the shortest bond being O7···H1′ (2.28 Å).

On the ligand side of the H-tube, single crystals of the same composition $[Ag(L)]ClO_4$, **2** are found. However, the unit cell dimensions are different in length and angles, **2** crystallizing in the monoclinic space group *C*2/*c* (no. 15).[13] Instead of forming molecular units in a ring-form, the loops (with two ligand molecules per two silver cations) in **1** open up to yield a single stranded helix where three ligand molecules are coordinated to two silver cations (Fig. 2). The chain thus obtained, ···L–Ag–L–Ag–L···, has the ligand again in a U-shaped conformation, all-*gauche*, similar to the ring described above for **1**. The silver ions are distributed along a zig-zag chain in the direction of the *b*-axis, with shortest Ag1–Ag1′ distances of 3.781(2) Å, excluding metal–metal interactions. The Ag1–N distances in **2** are 2.158(7) and 2.161(6) Å for N2 and N1, respectively. The two pyridine rings within one ligand are at their shortest distance [4.39(1) Å] measured from N1 to N2, thus excluding π-stacking. The N–N distance through space between two different ligands is 3.59(1) Å with the centers of these pyridine rings 3.742(6) Å apart, and almost completely offset by 3.4 Å, excluding efficient π–π interactions. The height of one full turn of the helix, measured from Ag1 to the next Ag1 in the chain, is 7.104 Å, corresponding to the *b*-parameter of the unit cell.

Whereas molecular boxes or rings as observed in **1** are well described,[15] single helical arrangements remain quite rare, even though they are highly interesting due to their inherent chirality.[8,16] Even rarer are examples for concomitant polymorphs, one of them having a helical structure. The compound $[\{HC(3\text{-}Phpz)_3\}Ag](BF_4)$ (pz = pyrazolyl) yields two polymeric polymorphs from the same solvent combination, but it is not clear from the description whether they crystallize simultaneously or in parallel assays.[17] Two polymeric polymorphs out of the same solution at room temperature are described for a Cu(I) compound.[18] A hexamer and a zig-zag-structure, but not a helix, are observed for a Cu(II) compound.[19] For other M(II) metal ions, temperature, solvent and pressure dependent polymorphism has been observed.[20] It has been discussed recently that the anion tunes the secondary self-assembly, leading to rings, helices or chains.[21] This can be excluded in our case. Another theory of ring-opening polymerization also does not fit in our case as both crystals occur at the same time.[22] In fact, in this case, a concentration effect can be proposed. On the side with $AgClO_4$ in water, Ag cations are in excess with respect to ligand L, so that fragments of $[AgL]^+$ are formed as ligand diffuses towards this compartment of the H-tube. In our polar solvents, the dissociation of the possible soft species $[Ag_2L]^{2+}$ to yield $[Ag_2L_2]^{2+}$ and $[Ag]^+$ is probably entropically favored, leading to an anti-cooperative effect. To confirm this hypothesis, formation constants of the different species will have to be determined in different solvents. On the other side, ligand L is in excess with respect to Ag^+, and fragments of the type $[Ag(L)_2]^+$ can be formed, which would lead to the helical structure upon polymerization with other such fragments or $[Ag(L)]^+$. The presence of such species in varying ratios as a function of time and concentration could be confirmed by electrospray mass spectrometry.

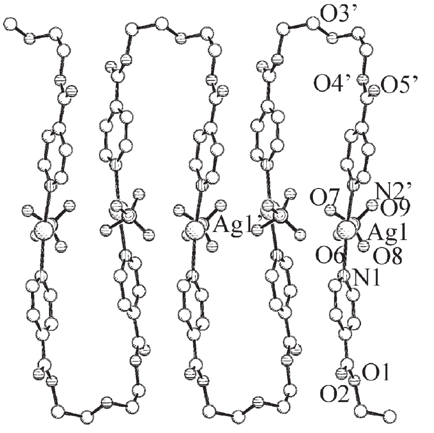

Fig. 2 Side-view of one helical single-strand structure of **2**, H-atoms omitted for clarity (symmetry operation (′) $-x + 0.5$, $y + 0.5$, $-z + 0.5$).

This is therefore the first case of supramolecular isomerism induced by concentration effects, both polymorphs coexisting in the same solution, where a ring and a helical Ag(I) compound are formed. After total diffusion, only the ring, compound **1**, is found, so that compound **2** can be considered as a kinetic product, whereas the ring forming isomer **1** is the thermodynamically more stable product. With other anions as counter ions, only the ring isomer has been obtained and observed so far, but this will be the subject of another publication.[23]

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Notes and references

† In an H-tube, 0.011 g (0.05 mmol) of $AgClO_4$ were dissolved in 5 ml of water and introduced into one side of the tube whereas the other was filled with 5 ml of a THF-solution containing 0.036 g (0.11 mmol) of ligand. The two solutions were put into contact with each other via a 1 : 10 mixture of water and THF. Single crystals of **1** were collected on the silver salt side, whereas compound **2** formed on the other side of the H-tube. Yields: 9.3 mg of **1** (0.018 mmol, 36% with respect to $AgClO_4$) and 11.4 mg of **2** (0.022 mmol, 45% with respect to $AgClO_4$). Elemental analysis for **1**: calculated: C 36.70, H 3.08, N 5.35%; found: C 36.01, H 3.16, N 5.07%. Elemental analysis for **2**: calculated: C 36.70, H 3.08, N 5.35%; found: C 35.86, H 3.25, N 4.91%. IR for **1** (KBr, cm^{-1}): 3092 (w), 2919 (s), 2852 (s), 2308 (vw), 1718 (vw), 1689 (w), 1580(w), 1449 (m), 1342 (m), 1252 (w), 1245 (m, sh), 1100 (m, sh), 825 (w), 810 (w, sh). IR of **2** (KBr, cm^{-1}): 3094 (w), 2953 (w), 1722 (s), 1610 (m), 1560 (m), 1447 (w), 1424 (m), 1340 (m), 1297 (s), 1242 (m), 1100 (m, sh), 812 (w, sh). ES-MS (crude reaction mixture): $[AgL]^+$ (424 *m*/*z*), $[Ag_2L(ClO_4)]^+$ (631), $[AgL_2]^+$ (740), $[Ag_2L_2(ClO_4)]^+$ (948).

1 S. R. Batten and R. Robson, *Angew. Chem. Int. Ed.*, 1998, **37**, 1460; A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. Schröder and M. A. Withersby, *Coord. Chem. Rev.*, 1999, **183**, 117; A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. Schroder, *Coord. Chem. Rev.*, 2001, **222**, 155–192.

2 G. R. Desiraju (Editor), *The Crystal as a Supramolecular Entity*, Wiley, New York, 1995 and refs. therein; R. Robson, B. F. Abrahams,

S. R. Batten, R. W. Gable, B. F. Hoskins and J. Liu, in *Supramolecular Architecture*, American Chemical Society, Washington, DC, 1992, ch. 19, p. 256.

3 L. R. Hanton and K. Lee, *J. Chem. Soc., Dalton Trans.*, 2000, 1161; N. Hong, W. Su, R. Cao, M. Fujita and J. Lu, *Chem. Eur. J.*, 2000, **6**, 427; L. Carlucci, D. M. Proserpio and S. Rizzato, *Chem. Eur. J.*, 2002, **8**, 1520 and refs. therein.

4 S. A. Barnett, A. J. Blake, N. R. Champness and C. Wilson, *Chem. Commun.*, 2002, 1640 and refs. therein.

5 J. Bernstein, R. J. Davey and J.-O. Henck, *Angew. Chem. Int. Ed.*, 1999, **38**, 3440–3461.

6 M. Schröder and N. R. Champness, in *Encyclopedia of Supramolecular Chemistry*, ed. J. L. Atwood and J. W. Steed, Dekker, New York, 2004, pp. 1420–1426; D. Braga, L. Brammer and N. R. Champness, *CrystEngComm*, 2005, **7**, 1–19.

7 J. Bernstein, in *Supramolecular Engineering of Synthetic Metallic Materials*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1999, pp. 23–40.

8 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629–1658.

9 K. M. Fromm, G. Bernardinelli, H. Goesmann, M.-J. Mayor-Lopez and J. Weber, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1685–1691.

10 K. M. Fromm, G. Bernardinelli and H. Goesmann, *Polyhedron*, 2000, **19**, 1783–1789.

11 K. M. Fromm, *Chem. Eur. J.*, 2001, **7**, 2236–2244.

12 K. M. Fromm and H. Goesmann, *Acta Crystallogr., Sect. C*, 2000, **56**, 1179–1180.

13 Single crystal data for **1**: $AgC_{16}H_{16}ClN_2O_9$, $M = 523.63$ g mol^{-1}, triclinic, space group $P\bar{1}$ (No. 2), $a = 7.190(1)$, $b = 12.074(2)$, $c = 12.078(2)$ Å, $\alpha = 112.54(3)$, $\beta = 102.27(3)$, $\gamma = 96.68(3)^\circ$, $V = 923.3(3)$ Å^3, $Z = 2$, $T = 240(2)$ K, $\rho = 1.883$ Mg m^{-3}, $\mu(MoK_\alpha) = 1.292$ mm^{-1}, $F(000) = 524$, 10734 reflections of which 5569 unique and 4391 observed, 278 parameters refined, GooF = 1.013, $R1 = 0.0568$, $wR2 = 0.1508$ for $I > 2\sigma(I)$ and $R1 = 0.0759$, $wR2 = 0.1732$ for all data. Single crystal data for **2**: $AgC_{16}H_{16}ClN_2O_9$, $M = 523.63$ g mol^{-1}, monoclinic, space group $C2/c$ (No. 15), $a = 23.631(5)$, $b = 7.104(1)$, $c = 25.554(5)$ Å, $\beta = 117.12(3)^\circ$, $V = 3818.7(1)$ Å^3, $Z = 8$, $T = 240(2)$ K, $\rho = 1.822$ Mg m^{-3}, $\mu(Mo_{K\alpha}) = 1.249$ mm^{-1}, $F(000) = 2096$, 7494 reflections of which 4216 unique and 2037 observed, 262 parameters refined, GooF = 0.971, $R1 = 0.0785$, $wR2 = 0.1818$ for $I > 2\sigma(I)$ and $R1 = 0.1549$, $wR2 = 0.2220$ for all data. The intensities from the single crystals of **1** and **2** were measured on a STOE IPDS-II diffractometer, equipped with monochromated MoK_α radiation, at 240K. The structures were solved by direct methods and refined by full matrix least-squares on F^2 with the SHELX-97 package.[24] All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms. CCDC 251188 (**1**) and 251189 (**2**). See http://dx.doi.org/10.1039/b506389b for crystallographic data in CIF or other electronic format.

14 K. M. Fromm, A. Robin, M. Meuwly, H. Goesmann and G. Bernardinelli, *CrystEngComm*, 2004, **6**, 336–343.

15 Rings: O.-S. Jung, Y.-A. Lee, Y. J. Kim and J. Hong, *Cryst. Growth Des.*, 2002, **2**, 497–499; O.-S. Jung, Y. J. Kim, Y.-A. Lee, S. W. Kang and S. N. Choi, *Cryst. Growth Des.*, 2004, **4**, 1, 23–24; M.-C. Brandys and R. J. Puddephatt, *Chem. Commun.*, 2001, 1508–1509; D. Braga, M. Polito, M. Bracaccini, D. D'Addario, E. Tagliavini, D. M. Proserpio and F. Grepioni, *Chem. Commun.*, 2002, 1080–1081; E. Lindner, R. Zong, K. Eichele, U. Weisser and M. Ströbele, *Eur. J. Inorg. Chem.*, 2003, 705–712; P. L. Caradoc-Davies and L. R. Hanton, *Dalton Trans.*, 2003, 1754–1758; J. C. Garrison, R. S. Simons, J. M. Talley, C. Wesdemiotis, C. A. Tessier and W. J. Youngs, *Organometallics*, 2001, **20**, 1276–1278; D. Braga, M. Polito, D. D'Addario, E. Tagliavini, D. M. Proserpio, F. Grepioni and J. W. Steed, *Organometallics*, 2003, **22**, 4532–4538; C. M. Hartshorn and P. J. Steel, *Inorg. Chem.*, 1996, **35**, 6902–6903; S. Chowdhury, M. G. B. Drew and D. Datta, *New. J. Chem.*, 2003, **27**, 831–835; T. Suzuki, H. Kotsuki, K. Isobe, N. Moriya, Y. Nakagawa and M. Ochi, *Inorg. Chem.*, 1995, **34**, 530–531.

16 Helices: P. L. Caradoc-Davies and L. R. Hanton, *Chem. Commun.*, 2001, 1098–1099; S. Sailaja and M. V. Rajasekharan, *Inorg. Chem.*, 2000, **39**, 4586–4590; Y.-B. Dong, J.-Y. Cheng, J.-P. Ma, H.-Y. Wang, R.-Q. Huang, D.-S. Guo and M. D. Smith, *Solid State Sciences*, 2003, **5**, 1177–1186; S. Qin, S. Lu, Y. Ke, J. Li, X. Wu and W. Du, *Solid State Sciences*, 2004, **6**, 753–755; C.-D. Wu, H. L. Ngo and W. Lin, *Chem. Commun.*, 2004, 1588–1589; S. P. Anthony and T. P. Radhakrishnan, *Chem. Commun.*, 2004, 1058–1059; Y.-T. Fu, V. M. Lynch and R. J. Lagow, *Chem. Commun.*, 2004, 1068–1069; J.-H. Yang, S.-L. Zheng, X.-L. Wu and X.-M. Chen, *Cryst. Growth Des.*, 2004, **4**, 831–836; A. Erxleben, *Inorg. Chim. Acta*, 2003, **348**, 107–114; A. J. Blake, N. R. Champness, P. A. Cooke, J. E. B. Nicolson and C. Wilson, *J. Chem. Soc., Dalton Trans.*, 2000, 3811–3819; F. Tuna, J. Hamblin, G. Clarkson, W. Errington, N. W. Alcock and M. J. Hannon, *Chem. Eur. J.*, 2002, **8**, 21, 4957–4964; G. Dong, H. Cheng, D. Chun-Ying, Q. Chun-Qi and M. Qing-Jin, *New J. Chem.*, 2002, **26**, 796–802; Y.-P. Cai, H.-X. Zhang, A.-W. Xu, C.-Y. Su, C.-L. Chen, H.-Q. Liu, L. Zhang and B.-S. Kang, *J. Chem. Soc., Dalton Trans.*, 2001, 2429–2434; Y. Kang, S. S. Lee, K.-M. Park, S. H. Lee, S. O. Kang and J. Ko, *Inorg. Chem.*, 2001, **40**, 7027–7031; A. Jouaiti, M. W. Hosseini and N. Kyritsakas, *Chem. Commun.*, 2003, 472–473; B. Schmaltz, A. Jouaiti, M. W. Hosseini and A. De Cian, *Chem. Commun.*, 2001, 1242–1243; M. J. Hannon, C. L. Painting, E. A. Plummer, L. J. Childs and N. W. Alcock, *Chem. Eur. J.*, 2002, **8**, 2225–2238; K.-M. Park, D. Whang, E. Lee, J. Heo and K. Kim, *Chem. Eur. J.*, 2002, **8**, 498–508; D. Whang, J. Heo, C.-A. Kim and K. Kim, *Chem. Commun.*, 1997, 2361–2362.

17 D. L. Reger, R. F. Semeniuc and M. D. Smith, *Eur. J. Inorg. Chem.*, 2003, 3480–3494.

18 S. Masoaka, D. Tanaka, Y. Nakanishi and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2004, **43**, 2530–2534.

19 H. Abourahma, B. Moulton, V. Kravtsov and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2002, **124**, 9990–9991.

20 I. S. Lee, D. M. Shin and Y. K. Chung, *Chem. Eur. J.*, 2004, **10**, 3158–3165; D. Braga, M. Polito, D. D'Addario and F. Grepioni, *Cryst. Growth Des.*, 2004, **4**, 1109–1112; D. V. Soldatov, G. D. Enright, J. A. Ripmeester, J. Lipkowski and E. A. Ukraintseva, *J. Supramol. Chem.*, 2001, **1**, 245–251; E. Tynan, P. Jensen, N. R. Kelly, P. E. Kruger, A. C. Lees, B. Moubaraki and K. S. Murray, *Dalton Trans.*, 2004, 3440–3447.

21 H.-J. Kim, W.-C. Zin and M. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 7009–7014.

22 E. Lozano, M. Nieuwenhuyzen and S. L. James, *Chem. Eur. J.*, 2001, **7**, 2644–2651.

23 J. L. Sague Doimeadios, A. Y. Robin and K. M. Fromm, unpublished results.

24 G. M. Sheldrick, SHELX-99, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1999.