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The First Linear Coordination Oligomer Linked by 4,4′-Bipyridine

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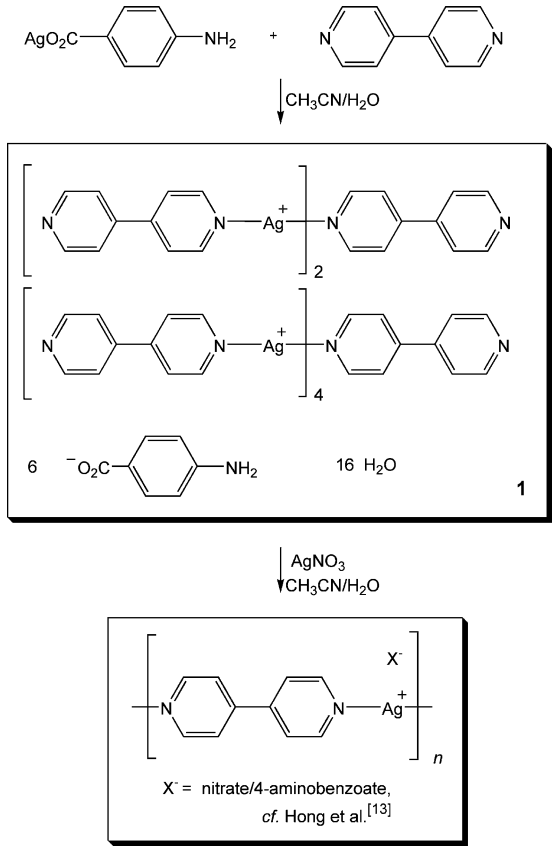
A unique coordination oligomer derived from bridging 4,4′-bipyridine (bipy) ligands was synthesized and characterized. Long linear $[Ag_4(bipy)_5]^{4+}$ tetracations, shorter $[Ag_2(bipy)_3]^{2+}$ dications and 4-aminobenzoate anions represent the major constituents. When silver nitrate was added to solutions of this salt, polymerization in high yield occurred.

Introduction

The optical, catalytic or magnetic properties of coordination polymers make them candidates for a plethora of potential applications.[1] The broad interest in this subject is reflected in an increasing number of publications during the last decade.[2] Active research is devoted to the structural chemistry of metal-containing polymers: about 11% of the structurally characterized organometallic and coordination compounds are polymeric.[3,4] 4,4′-Bipyridine (bipy) plays an important role among the organic linkers between metal cations. The relevance of this ligand for the construction of coordination polymers was recently reviewed by Biradha et al.[5] We encountered single-crystal to single-crystal reactions in surprisingly dynamic coordination polymers involving 4,4′-bipyridine.[6,7] To date, about 800 metal-containing derivatives of this organic ligand have been studied by diffraction methods; a large majority of these compounds contain bridging bipyridine molecules, but structures with a terminal bipy connected to a single metal cation through only one of the N donors have also been described.[8] Chemists intuitively associate polymers with oligomers as obvious intermediates; to the best of our knowledge, no linear coordination oligomer based on 4,4′-bipyridine, that is, no complex of finite nuclearity containing more than two metal atoms linked by this ligand, has ever been structurally characterized.[9] In this contribution, we wish to report the synthesis and characterization of the first oligocation based on bridging and terminal 4,4′-bipy ligands.

Results and Discussion

Silver mono- or dicarboxylates and difunctional N donor ligands such as ethylendiamine,[10–12] 4,4′-bipyridine[13–21] or 1,2-diaminocyclohexane[22,23] have been reported to form polycationic $[Ag(ligand)^+]_\infty$ chains that are potentially cross-linked through weaker interactions such as argentophilic contacts or long Ag–O bonds. In contrast to this predictable behaviour, the reaction between silver 4-aminobenzoate and 4,4′-bipyridine results in the unexpected and unprecedented formation of **1**, which is a rather complex solid. Single-crystal X-ray diffraction showed that



Scheme 1. Synthesis of **1** and polymerization upon addition of $AgNO_3$.

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its building blocks comprise a dication $[Ag_2(bipy)_3]^{2+}$, a tetracation $[Ag_4(bipy)_5]^{4+}$, 6 4-aminobenzoate anions and 16 water molecules (Scheme 1).

The two cationic residues in the asymmetric unit are represented in Figure 1a,b: Ag–N bonds lead to the expected almost linear coordination of the Ag^I centres, and deviations due to additional considerably longer and weaker interactions between the silver centres and the aqua or carboxylato oxygen atoms are also apparent. Five of the Ag^I centres interact with two O donor ligands, whereas the sixth Ag^I centre interacts with only one O donor ligand; the distances of these interactions fall in the range between 2.45 and 2.69 Å. Among the 16 water molecules in the asymmetric unit of **1**, 4 play a special role. Not only do they coordinate to the silver cations, but they also form hydrogen-bonding bridges with the dangling ends of the oligocations; the uncoordinated N atoms of the terminal bipy ligands act as acceptors. The long $[Ag_4(bipy)_5]^{4+}$ cations are crosslinked by bridging carboxylato oxygen atoms from two anions (Figure 1c).

The crosslinked longer residues and the discrete shorter cationic residues in **1** extend along the crystallographic *c* direction with stacking distances of approximately 3.5 Å. Matching torsion angles between the aryl rings along both polymer chains ensure a largely coplanar arrangement along the stacking direction (Figure 2).

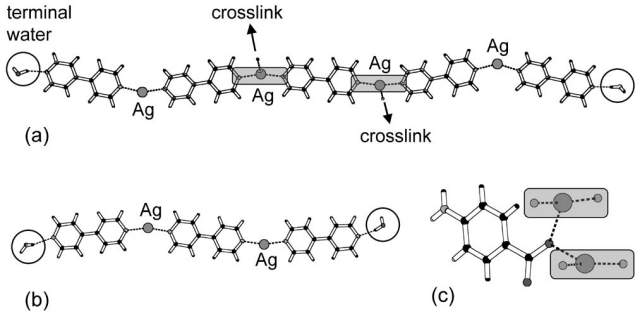

Figure 1. Tetracation $[Ag_4(bipy)_5]^{4+}$ (a) and dication $[Ag_2(bipy)_3]^{2+}$ (b) in **1**; the water molecules that are hydrogen bonded to the terminal pyridyl rings interact with metal centres in neighbouring residues through rather long coordinative bonds [Ag–O min 2.617(3), max 2.678(4) Å]; Ag···O interactions are not shown. (c) Geometry of a carboxylate crosslink between adjacent tetracations; the two symmetrically independent Ag···Ag distances are 3.2811(11) and 3.3773(11) Å.

Hydrogen bonding in **1** is limited by the number of H donors: The 16 water molecules and the 6 amino groups result in a total of 44 potential donor hydrogen atoms; the structure comprises a larger number of suitable classical acceptor sites, namely those associated with the 12 carboxylato and 16 water oxygen atoms, in addition to the 4 bipy N atoms. Of the 44 donor H atoms, 40 find an electronegative acceptor atom in reasonable geometry, and the remaining four, all of them aryl-bonded amino hydrogen atoms, point towards the centres of the aromatic rings in the adjacent anions. A detailed analysis of short interresidue contacts in **1** is provided in the Supporting Information.

As outlined above, 4 of the 16 water molecules in the asymmetric unit of **1** simultaneously participate in two different interactions with the ionic residues of the structure and both are hydrogen bonded and weakly metal coordinated. DSC and thermogravimetric studies show that the water molecules from **1** are released in two steps and in a 3:1 ratio upon heating. It is tempting to associate the second dehydration step with the loss of the more tightly bonded water molecules that terminate the oligocations.

Conclusions

Compound **1** was obtained in high yields and should not simply be regarded as a singular novel structure. Solutions of the compound show the chemical reactivity expected for oligomers. The residues contributing to the formation of **1**, namely, 4-aminobenzoate, Ag^I cations and the 4,4′-bipyridine ligand, in the additional presence of nitrate anions, take part in a different and less spectacular reaction described recently by Hong et al.[13] These authors obtained a one-dimensional coordination polymer of composition $\{[Ag(4,4'\text{-bipy})(H_2O)](aba)_{0.5}(NO_3)_{0.5}\cdot(H_2O)_{0.5}\}_\infty$ with infinite polycationic chains. The nature of the anions is decisive for the outcome of the reaction. When silver nitrate is added to a solution of oligomeric compound **1** in acetonitrile/water (Scheme 1), the above-mentioned coordination polymer precipitates almost quantitatively. The oligocations in **1** do not represent a dead end; rather, they are intermediates on the way to polymers that can be trapped under a favourable combination of counteranions.

Experimental Section

Silver 4-aminobenzoate [Ag(aba)] was prepared from potassium benzoate and silver nitrate. Satisfactory microanalytical data were

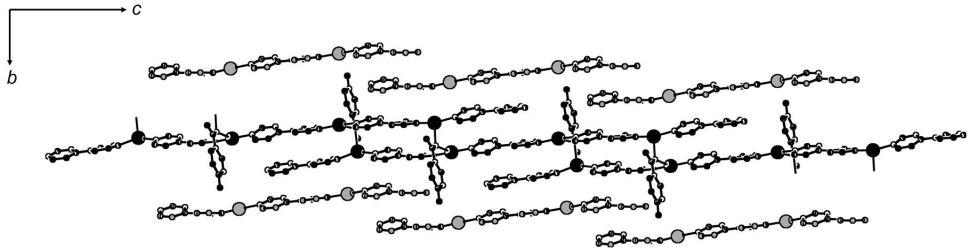

Figure 2. Arrangement of the anion-crosslinked tetracations (black) and the discrete dications (grey) in the crystal structure of **1**; the remaining four anions and the water molecules are omitted.

obtained. The structure of this salt was determined by Amiraslanov et al.[24]

1: A solution of 4,4′-bipyridine (0.124 g, 0.8 mmol) in CH_3CN (5 mL) was added to a solution of Ag(aba) (0.146 g, 0.6 mmol) in acetonitrile/water (1:1), and the mixture was stirred for 30 min at room temperature and then filtered. After 2 d of slow evaporation at room temperature, light-yellow crystals suitable for X-ray diffraction precipitated. Yield: 0.225 g [75%, based on Ag(aba)]. Compound **1** is stable when exposed to light. $C_{122}H_{132}Ag_6N_{22}O_{28}$ (3001.72): calcd. C 48.82, H 4.43, N 10.27; found C 48.68, H 4.46, N 10.20. ^{1}H NMR (400 MHz; CD_3CN/D_2O, 1:1): δ = 6.72 (m, 6×2 H, 4-aminobenzoate), 7.68 (m, 6×2 H, 4-aminobenzoate), 7.81 (m, 8×4 H, 4,4′-bipyridine), 8.67 (m, 8×4 H, 4,4′-bipyridine) ppm. The spectrum confirms the composition of the bulk and the expected integration result of 24 H (6 anions) versus 64 H (8 bipyridine moieties).

Compound **1** was dehydrated in two steps, and the second step was close to decomposition. Around 100 °C, a weight loss of 7.8% (calculated for the loss of 12 H_2O 7.2%) occurred and around 120 °C, a weight loss of 2.6% (calculated for the loss of 4 H_2O 2.4%) occurred (Supporting Information).

The IR spectrum of **1** and that of the coordination polymer reported by Hong et al.[13] differ significantly in the region between 1420 and 1350 cm^{-1}. In contrast to the polymer, **1** does not contain NO_3^- anions.

Single-Crystal X-ray Structure Determination: Data were collected with a Bruker Smart APEX CCD detector (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator) with a D8 goniometer. Temperature was controlled with an Oxford Cryosystems Series 800 instrument. Intensities were integrated with SAINT[25] and corrected for absorption with SADABS.[26] Structures were solved by direct methods (SHELXS-97)[27] and refined on F^2 with SHELXL-97.[28]

Crystal Data for 1: Monoclinic space group $P2_1$, a = 18.2356(11) Å, b = 14.0626(8) Å, c = 23.6767(14) Å, β = 95.988(2)°, V = 6038.5(6) Å^3, Z = 2; T = 130 K; refinement of 1604 parameters based on 29526 independent out of totally 70319 reflections converged at R_1 = 0.0506, wR_2 = 0.0994, GOF = 1.000. In view of the inversion twinning [Flack parameter[29] 0.539(15)] encountered for the crystal documented here, intensity data on a second crystal were collected and a Flack parameter of 0.351(18) was obtained. CCDC-657268 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystal data and structure refinement, Ag coordination and intermolecular interactions, thermal analysis, polymerization and photographs of crystals.

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[1] C. Janiak, *Dalton Trans.* **2003**, 278.
[2] A. Y. Robin, K. M. Fromm, *Coord. Chem. Rev.* **2006**, *250*, 2127.
[3] According to the CSD (cf. ref.[4]), V.5.28, including the update of Jan 2007, ca. 18000 structures out of ca. 170000 error-free organometallic and coordination compounds with 3D coordinates were polymeric.
[4] F. Allen, *Acta Crystallogr., Sect. B* **2002**, *58*, 380.
[5] K. Biradha, M. Sarkar, L. Rajput, *Chem. Commun.* **2006**, 4169.
[6] C. Hu, U. Englert, *Angew. Chem. Int. Ed.* **2005**, *44*, 2281.
[7] C. Hu, U. Englert, *Angew. Chem. Int. Ed.* **2006**, *45*, 3457.
[8] A search in the CSD (see refs.[3,4]) resulted in 61 error-free terminal bipy structures without disorder for which 3D coordinates were available.
[9] Dinuclear compounds involving both bridging and terminal 4,4′-bipy ligands were described in the following publications: a) X.-J. Lin, Z. Shen, Y.-Z. Li, H. Uno, Y. Song, H.-J. Xu, X.-Z. You, *J. Coord. Chem.* **2005**, *58*, 1139; b) J. T. Sampanthar, J. J. Vittal, *J. Chem. Soc. Dalton Trans.* **1999**, 1993; c) S. Gao, J.-W. Liu, L.-H. Huo, H. Zhao, S. W. Ng, *Acta Crystallogr., Sect. E* **2004**, *60*, m1590; d) M. Aoyagi, K. Biradha, M. Fujita, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1369. Cyclic oligomers have been described: The CSD (see refs.[3,4]) compiles 15 examples of molecular squares $M_4(bipy)_4$, and an $Os_6(bipy)_6$ ring has been characterized by Y. L. Cho, H. Uh, S.-Y. Chang, H.-Y. Chang, M.-G. Choi, I. Shin, K.-S. Jeong, *J. Am. Chem. Soc.* **2001**, *123*, 1258.
[10] H.-L. Zhu, X.-J. Sun, D.-Q. Wang, *Z. Kristallogr. New Cryst. Struct.* **2003**, *218*, 30.
[11] Z. L. You, L. Yang, Y. Zou, W. J. Zeng, W. S. Liu, H. L. Zhu, *Acta Crystallogr., Sect. C* **2004**, *60*, m117.
[12] A. Usman, H. K. Fun, S. Chantrapromma, H. L. Zhu, X. J. Wang, *Acta Crystallogr., Sect. C* **2003**, *59*, m97.
[13] R. Wang, M. C. Hong, J. Luo, F. Jiang, L. Han, Z. Lin, R. Cao, *Inorg. Chim. Acta* **2004**, *357*, 103.
[14] L. Ye, Y. Wu, *Acta Crystallogr., Sect. E* **2005**, *61*, m1894.
[15] J. T. Sampanthar, J. J. Vittal, *Cryst. Eng.* **2000**, *3*, 117.
[16] M.-L. Tong, X.-M. Chen, S. W. Ng, *Inorg. Chem. Commun.* **2000**, *3*, 436.
[17] D. Sun, R. Cao, Y. Sun, W. Bi, X. Li, Y. Wang, Q. Shi, X. Li, *Inorg. Chem.* **2003**, *42*, 7512.
[18] G. A. Bowmaker, Effendy, K. C. Lim, B. W. Skelton, D. Sukarianingsih, A. T. White, *Inorg. Chim. Acta* **2005**, *358*, 4342.
[19] D.-Q. Zhang, W.-H. Zhang, Q.-F. Xu, J.-P. Lang, S. W. Ng, *Acta Crystallogr., Sect. E* **2004**, *60*, 1256.
[20] F. Li, T. Li, D. Yuan, L. Lv, R. Cao, *Inorg. Chem. Commun.* **2006**, *9*, 691.
[21] Y. Wang, U. Englert, unpublished results.
[22] J.-C. Lee, H. Takahashi, Y. Matsui, *Z. Kristallogr. New Cryst. Struct.* **2005**, *220*, 493.
[23] I. Kalf, M. Braun, Y. Wang, U. Englert, *CrystEngComm* **2006**, *8*, 916.
[24] R. Amiraslanov, B. T. Usubaliev, G. N. Nadzhafov, A. A. Musaev, E. M. Movsumov, K. S. Mamedov, *Zh. Strukt. Khim.* **1980**, *21*, 112.
[25] Bruker AXS, *SAINT+: Program for Reduction of Data Collected on Bruker CCD Area Detector Diffractometer V. 6.02*, Bruker AXS Inc., Madison, USA, **1999**.
[26] G. M. Sheldrick, *SADABS: Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, **1996**.
[27] G. M. Sheldrick, *SHELXS97: Program for Crystal Structure Solution*, University of Göttingen, **1997**.
[28] G. M. Sheldrick, *SHELXL97: Program for Crystal Structure Refinement*, University of Göttingen, **1997**.
[29] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876.

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