STRUCTURAL AND THERMAL STUDY OF A NEW COORDINATION POLYMER POLY-BIS (μ_2 -BUTANE-1,2-DIYL BIS (PYRIDINE-3-CARBOXYLATE) K²N,SILVER(I) TETRAFLUOROBORATE

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ABSTRACT

Reaction of L (L=butane-1,2-diyl bis(pyridine-3-carboxylate) with AgBF₄ in a 1:1 ratio afforded crystals of [Ag(L)(BF₄)]_n which proved to be a one-dimensional linear polymeric chain. This compound crystallizes in the space group C2/c. In the crystal structure the linear chains are connected to another one via hydrogen bonds involving C15 as the donor atom, and O1 of the carboxylate group as the acceptor atom, thereby generating R₂²(20) centrosymmetric rings to form a two-dimensional supramolecular aggregate. The thermogravimetric analysis shows that this compound is thermally stable up to 298 °C. The decomposition process is produced in one stage. The weight loss occurs from 298 to 780 °C, which is attributable to the complete removal of the ligand molecule and BF₄ anion.

INTRODUCTION

The rational design and construction of functional coordination polymers have recently witnessed explosive growth in the areas of inorganic chemistry, coordination chemistry, crystal engineering, and materials science, not only due to their intrinsic aesthetic value but also to their potential applications in catalysis, gas storage, molecular adsorption, optical and magnetic materials¹⁻⁵. In general, the construction of these polymers is influenced by many factors such as the coordination geometry of metal center, the nature of the ligand, solvent, template, counter anions, temperature, and other factors. Among these, the judicious selection of appropriate ligands plays a key role in the manipulation of the structures of coordination polymers^{6,7}. Although the overall structure is predominantly controlled by the coordination preferences of the transition metal and the ligand building blocks, more subtle effects such as anion control and π - π stacking interactions⁸⁻¹⁰ have also been seen to have a profound effect upon the network topology. Herein, we report the synthesis, crystal structure and the thermal study of a new coordination polymer, formed by the reaction of the ditopic flexible butane-1,4-diyl-bis(pyridine-3-carboxylate) ligand¹⁵ (Scheme 1) with the silver tetrafluoroborate salt.

Scheme 1. Schematic structure of L (L = butane-1,4-diyl-bis(pyridine-3-carboxylate)).

EXPERIMENTAL

All chemicals used in this work were analytical reagent grade and employed as supplied without further purification, except the ligand which was synthesized by us, see Scheme 2. The ligand L was prepared in 75% yield, as a white solid by reaction of 1,4-butanediol and nicotinic chloride, and was characterized by FTIR & UV- vis spectroscopy and by x-ray crystallography on single crystal¹⁵.

Scheme 2. Reagents and reaction conditions for the synthesis of L.

Synthesis: Single crystals suitable for X-ray diffraction study for the title compound were obtained from a AgBF₄ solution (39 mg, 0.2 mmol) in H₂O (10 ml), which was added to a CH₃CN (10 ml) solution of L (30.0 mg, 1 mmol). The clear solution was kept for many days at room temperature until crystals formed. Colourless crystals of [Ag(L)(BF₄)]_n were collected with approximately 75% yield.

X- ray Structure Analysis:

Single crystal analysis data were collected on a Stoe IPDS-II two-circle Diffractometer with MoK α radiation. Data collection: X-Area¹⁶; cell refinement X-Area¹⁶; data reduction: X-Area¹⁶. Program used to solve structure, program(s) used to refine structure: SHELXL97¹⁷; molecular graphics: XP in SHELXTL-Plus¹⁷ & OLEX2¹⁸, software used to prepare material for publication: SHELXL97¹⁶. Crystal dimension of C₁₆H₁₆AgN₂O₄BF₄ 0.33x 0.29x0.27 mm³. All H atoms were located in difference maps and their positions and isotropic displacements parameters of 1.2 times those of the attached atoms. Additional data collection and refinement details are given in Table 1. Supplementary information: Crystallographic data (excluding structure factors) for the structural analysis have been deposited in the Cambridge Crystallographic Data Centre, CCDC 916340. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre; Postal Address : CCDC, 12 Union Road , Cambridge CB21EZ, UK, Telephone: (44) 01223 762910, Fax: (44) 01223 336033, e-mail: deposit@ccdc.cam.ac.uk.

Spectral Characterization: FTIR spectra were obtained with a Nicolet Avatar 330 spectrometer, using KBr pellets, in the range 4000–400 cm⁻¹. The UV-vis spectra were recorded on an Perkin Elmer Lambda 20 Spectrophotometer with diffuse reflectance sphere in the range of 200–400 nm in the solid state at room temperature.

Thermogravimetric study: Thermal stability (TG-DTA) studies were performed with a DTG-60H (Shimadzu) thermal analyzer from room temperature to 800 °C, with a heating rate of 10 °C /min.

Table 1. Crystal data and structure refinement for $C_{16}H_{16}AgBF_4N_2O_4$.

Empirical formula	$C_{16}H_{16}AgBF_4N_2O_4$	
Formula weight	494.99	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 17.416(2) Å b = 13.1378(14) Å c = 7.8246(10) Å	$\alpha = 90^\circ$ $\beta = 96.566(10)^\circ$ $\gamma = 90^\circ$
Volume	1778.6(4) Å ³	
Z	4	
Density (calculated)	1.849 Mg/m ³	
Absorption coefficient	1.200 mm ⁻¹	
F(000)	984	
Crystal size	0.33 x 0.29 x 0.27 mm ³	
Theta range for data collection	3.86 to 25.62°	
Index ranges	-21 ≤ h ≤ 18, -15 ≤ k ≤ 15, -9 ≤ l ≤ 9	
Reflections collected	6065	
Independent reflections	1665 [R(int) = 0.0396]	
Completeness to theta = 25.00°	99.2 %	
Absorption correction	Semi-empirical from equivalents ¹⁹⁻²⁰	
Max. and min. transmission	0.7377 and 0.6929	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1665 / 0 / 138	
Goodness-of-fit on F ²	1.116	
Final R indices [I > 2σ(I)]	R ₁ = 0.0246, wR ₂ = 0.0639	
R indices (all data)	R ₁ = 0.0255, wR ₂ = 0.0645	
Extinction coefficient	0.0034(6)	
Largest diff. peak and hole	0.547 and -0.541 e.Å ⁻³

Figure 1. FT-IR spectrum for the title compound. **Figure 2.** Diffuse reflectance spectra of L and $[(AgL)BF_4]_n$.

RESULTS AND DISCUSSION

The characteristic feature of the FTIR spectra of L and the coordination polymer is the strong absorption around 1720-1727 cm^{-1} which corresponds to the stretching vibration of the C=O group. The absorption band around 1601-1610 cm^{-1} corresponds to the stretching vibration of the C=N group in the pyridine ring. The relatively high frequency for the C=N group with respect to the free ligand (1589 cm^{-1}) suggests that the nitrogen atom of the C=N group in the pyridine ring participates in the coordination to the metal atom, which is confirmed by X-ray crystallography. In the title compound, the characteristic band appearing at 1056 cm^{-1} indicates the existence of the BF_4^- anion, Figure 1.

The electronic absorption spectrum of the title compound was measured in the solid state at room temperature (Figure 2). When the silver ions are coordinated, a red shift relative to the absorption bands corresponding to L is

observed in the spectrum of title compound, and an additional absorption band appears around 322-326 nm, probably due to a transition of a metal to ligand charge transfer state (MLCT)^{14a}.

Reaction of L with $AgBF_4$ in a 1:1 ratio afforded crystals of $[Ag(L)(BF_4)]_n$, which proved to be the one-dimensional linear polymeric chain, shown in Figure 3(a). As shown in Figure 3(c), each Ag(I) center is coordinated by two symmetry-related N and F atoms. The coordination environment of the silver(I) ion is pseudo-square planar and with a deviation of Ag(I) from the least-squares plane through the two N and two F atoms of 0.310 Å, Table 2. The Ag-F distance is the van der Waals' limit. The Ag-N bond distance is 2.151(2) Å, typical value for Ag(I)-N(py) coordination distances¹¹⁻¹³. The bond angle N-Ag(I)-N of 167.46(11)° is indicative of the presence of a distortion from linearity. The Ag(I)-Ag(I) separation across L is 18.259(2) Å.

Figure 3. (a) Part of the crystal structure of the title compound, showing one dimensional linear polymeric chains. (b) Connections via hydrogen bonds (Symmetry code: (i) $x, y, -1 + z$).

Figure 3. (c) Coordination sphere of the Ag (I) ion (symmetry codes: #2 $-x, y, -z+1/2$; #3 $-1/2+x, 1/2-y, -1/2+z$; #4 $1/2-x, 1/2-y, 1-z$)

In the compound, the linear chains are connected between them via hydrogen bonds involving C15, as donor atom and O1 atom of the carboxylate group as acceptor, thereby generating $R_2^2(20)$ centrosymmetric rings¹⁴ to form a two-dimensional supramolecular aggregate, Figure 3(b) (H15...O1 ($x, y, -1+z$) 2.44 Å, C15...O1 3.147(3) Å, C15-H15...O1 131°). In the title compound the butane moiety of L losses the trans conformation relative to the ligand free¹⁵.

Figure 4 shows the thermal behavior of the studied compound. The thermogravimetric analysis shows that the compound is thermally stable up to 298 °C. The decomposition process is produced in one stage. The weight loss occurs from 298 to 780 °C, which is attributable to the complete removal of the ligand molecule and BF_4^- anion (calcd. 78.2%; found 77.8%). The final residue is attributable to a silver compound of unknown composition.

Figure 4. TGA curve.

Table 2. Selected bond lengths [Å] and angles [°] for $\text{C}_{16}\text{H}_{16}\text{AgBF}_4\text{N}_2\text{O}_4$.

Ag(1)-F(1) ^{#3}	2.864(2)	N13-Ag1-F1 ^{#4}	90.30 (8)
N13 ^{#2} -Ag1-F1 ^{#3}	87.34 (8)	F1 ^{#3} -Ag-F1 ^{#4}	158.28 (8)

Symmetry codes: #1 $-x+1, y, -z+1/2$; #2 $-x, y, -z+1/2$; #3 $-1/2+x, 1/2-y, -1/2+z$; #4 $1/2-x, 1/2-y, 1-z$

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REFERENCES

- (a) J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp. *Chem. Soc. Rev.* **38**, 1450, (2009) (b) Y. Liu, W. M. Xuan, Y. Cui. *Adv. Mater.* **22**, 4112, (2010)
- (a) S. R. Batten, K. S. Murray. *Coord. Chem. Rev.* **246**, 103 (2003) ; (b) X. H. Bu, M. L. Tong, H. C. Chang, S. Kitagawa, S. R. Batten. *Angew. Chem. Int. Ed.* **43**, 192, (2003).
- (a) B. Moulton, M. J. Zaworotko. *Chem. Rev.* **101** (2001) 1629-1658. (b)

- K. Kim, *Chem. Soc. Rev.*, **31** (2002) 96- (c) R. J. Hill, D. L. Long, N. R. Champness, P. Hubberstey, M. Schröder. *Acc. Chem. Res.* **38**, 335, (2005).
4. (a) S. R. Batten, R. Robson. *Angew. Chem. Int. Ed.* **37**, 1460, (1998); (b) X. H. Bu, W. Chen, S. L. Lu, R. H. Zhang, D. Z. Liao, W. M. Bu, M. Shionoya, F. Brisse, J. Ribas. *Angew. Chem.* **113**, 3301, (2001)
 5. (a) X. L. Wang, C. Qin, S. X. Wu, K. Z. Shao, Y. Q. Lan, S. Wang, D. X. Zhu, Z. M. Su, E. B. Wang. *Angew. Chem. Int. Ed.* **48**, 5291, (2009); (b) Y. B. Zhang, W. X. Zhang, F. Y. Feng, J. P. Zhang, X. M. Chen. *Angew. Chem. Int. Ed.* **48**, 5287, (2009)
 6. (a) D. L. Caulder, K. N. Raymond. *Acc. Chem. Res.* **32**, 975, (1999); (b) Y. L. Bai, J. Tao, W. Wernsdorfer, O. Sato, R. B. Huang, L. S. Zheng. *J. Am. Chem. Soc.* **128**, 16428, (2006)
 7. (a) J. S. Fleming, K. L. V. Mann, C. A. Carraz, E. Psillakis, J. V. Jeffry, J. A. McCleverty, M. D. Ward. *Angew. Chem. Int. Ed.* **37**, 1279, (1998); (b) G. F. Swiegers, T. J. Malefetse. *Chem. Rev.* **100**, 3483 (2000)
 8. (a) D. M. P. Mingos, A. L. Rohl. *Inorg. Chem.* **30**, 3769, (1991); (b) K. A. Hirsch, S. R. Wilson, J. S. Moore. *Inorg. Chem.* **36**, 2960, (1997)
 9. (a) K. Biradha, K. V. Domasevitch, B. Moulton, C. Seward, M. J. Zaworotko. *Chem Commun.* (1999) 1327-1328 (b) M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubberstey, W.-S Li, M. Schroder. *Angew. Chem. Int. Ed. Engl.* **36**, 2327, (1997)
 10. I. Brito, J. Vallejos, A. Cárdenas, M. López-Rodríguez, M. Bolte, J. Llanos. *Inorg. Chem. Comm.* **14**, 897, (2011)
 11. R. L. LaDuca Jr., R.S. Rarig Jr, P.J. Zapf, J. Zubieta. *Solid State Sci.* **2**, 39, (1998)
 12. A.N. Khlobystov, A. J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schröder. *Coord. Chem. Rev.* **222**, 155, (2001)
 13. (a) M. Munakata, L.P. Wu, T. Kuroda-Sowa. *Bull. Chem. Soc. Jpn.* **70**, 1727, (1997); (b) A. Bondi. *J. Phys. Chem.* **68**, 441, (1964); (c) A.J. Blake, N.R. Champness, M. Crew, S. Parsons. *New J. Chem.* **23**, 13, (1999) (d) L. Pan, E.C. Woodlock, X. Wang, K.-C. Lam, A.L. Reingold. *Chem. Commun.* 1762, (2001) (e) L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi. *Inorg. Chem.* **37**, 5941, (1998); (f) M.-L. Tong, X.-M. Chen, B.-H. Ye, S.W. Ng. *Inorg. Chem.* **37**, 5278 (1998)
 14. J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang. *Angew. Chem. Int. Ed. Engl.* **34**, 1555, (1995)
 - 14^a. (a) X. J. Zhang, L. P. Jin, S. Gao. *Inorg. Chem.* **43**, 1600, (2004); (b) J. Yang, Q. Yue, G. Li, J. J. Cao, G. H. Li, J. S. Chen. *Inorg. Chem.* **45**, 2857, (2006); (c) A. Thirumurugan, S. J. Natarajan. *Chem. Soc., Dalton Trans.* 2923, (2004) (e) M.-S. Wang, S.-P. Guo, Y. Li, L.-Z. Cai, J. -P. Zou, G. Xu, W.-W. Zhou, F.-K. Zheng, G.-C. Gou. *J. Am. Chem. Soc.* **131**, 13572, (2009)
 15. J. Vallejos, I. Brito, A. Cárdenas, M. Bolte. *Acta Cryst.* **E68**, o2007, (2012)
 16. Stoe & Cie (2001). X-Area. Stoe & Cie. Darmstadt, Germany.
 17. G.M. Sheldrick. *Acta Cryst.* **A64**, 112, (2008)
 18. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann. OLEX2: A complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **42**, 339, (2009)
 19. A. L. Spek. *Acta Cryst.* **D65**, 148, (2009)
 20. R. H. Blessing. *Acta Cryst.* **A51**, 33, (1995)