Single crystal structural characterization of trichlorotetrapyridylbismuth(III) and its pyridine solvate

Jennifer N. Murphy,[a] Francesca M. Kerton,[a] and Louise N. Dawe*[a,b]

* Corresponding Author

Phone: 1-519-884-0710 ext. 4963

Fax: 1-519-746-0677

E-Mail: ldawe@wlu.ca

[a] Department of Chemistry, Memorial University of Newfoundland, St. Johns, NL, A1B 3X7, Canada

[b] Permanent address: Department of Chemistry, Wilfrid Laurier University, 75 University Avenue West, Waterloo, ON, N2L 3C5, Canada

Abstract

Pentagonal bipyramidal $(C_5H_5N)_4BiCl_3$ and its pyridine solvate are reported. The $(C_5H_5N)_4BiCl_3$ complex exhibits both intra- and intermolecular π-π stacking, while the pyridine solvate does not, but does contain four formula units in the asymmetric unit. A comparison between the coordination geometry of these solvation isomers and a series of isostructural lanthanide complexes is discussed.

Keywords

solvate; bismuth; pyridine complexes; chloride ligands; π–interactions

Introduction

As part of an ongoing study towards the development and characterization of new environmentally benign catalytic systems, bismuth(III) chloride was identified as a starting material of interest. Unlike neighbouring heavy metals on the periodic table, bismuth exhibits low toxicity, and bismuth(III) triflate has already been used extensively as a catalyst for various organic processes.[1]

The crystal structure of bismuth chloride was reported by Nyburg *et al* in 1971.[2] Each bismuth atom exhibited strong coordination to three chlorine atoms (2.468 – 2.518 Å) in a distorted trigonal pyramidal geometry, with a further five longer interactions (3.216 – 3.450 Å) to chlorine atoms which bridged to other bismuth centres. The overall eight coordinate geometry was approximately trigonal prismatic, with bismuth lying more closely to the base of the prism, which consisted of the three strongly bound chlorines, rather than directly in the centre of the prism. A comprehensive discussion of various coordination modes for complexes of BiX_3 (where X = Cl, I, Br) with pyridine (py; and pyridine derivatives, L) has been reported by Norman [3], where *fac*- and *mer*- BiX_3L_3 octahedral complexes, and five-coordinate, square-based pyramidal complexes are highlighted.

In the current study, we report our attempts to synthesize a simple complex containing $BiCl_3$ with *N*-donors (pyridine) and *O*-donors. *O*-coordination to $BiCl_3$ from crown ethers is known [4], with reported geometries ranging from an approximately C_4-symmetric seven-coordinate half-sandwich with 12-crown-4 [4a] to eight-coordinate bicapped trigonal prismatic for 15-crown-5 and benzo-15-crown-5, where one *Cl*- and one *O*-donor occupy the apical positions. [4b] Another report includes a larger crown ether (dibenzo-24-crown-8) that adopted a sigmoidal conformation, yielding two O_5-coordination pockets, with two bridging oxygen atoms, containing two bicapped trigonal prismatic Bi centres. [4f] As in the structure for simple $BiCl_3$, in these crown ether complexes the $BiCl_3$ unit maintains its pyramidal geometry. In our work we endeavoured to coordinate $BiCl_3$ with 7,10-dioxa-3,14-diazabicyclo[14.3.1]icosa-1(20),16,18-triene-2,15-dione, which has been previously identified as a possible metal sensor. [5] This macrocycle exhibited limited solubility in most solvents except pyridine, therefore, attempts to complex $BiCl_3$ and the macrocycle in pyridine were pursued. This yielded crystals of the Z' = 4 structure, trichlorotetrapyridylbismuth(III) pyridine disolvate (**2**). Recrystallizing $BiCl_3$ in pyridine, with no macrocycle present, yielded the lattice-solvent-free, Z' = 1, trichlorotetrapyridylbismuth(III) (**1**) instead of the high Z' structure, **2**. The lattice parameters for **1** have been previously reported by Norman [3], however, in that report the authors state that due to disorder, the structure was not of sufficiently high quality to be described in detail. Herein, the structural details are presented.

Synthesis

$BiCl_3$ was purchased from Alfa-Aesar and used without further purification. Pyridine was dried over CaH_2 and distilled prior to use. Manipulations were carried out under an inert nitrogen atmosphere using an MBraun Labmaster glovebox equipped with a freezer.

Trichlorotetrapyridylbismuth(III), $(C_5H_5N)_4BiCl_3$ (**1**): 2 g (0.6 mmol) of $BiCl_3$ was dissolved in 1.5 mL of pyridine to give a pale orange solution. The solution was stored overnight at −35 °C during which time colourless, small, irregular platelets formed, that were examined by X-ray diffraction.

Trichlorotetrapyridylbismuth(III) pyridine disolvate, $(C_5H_5N)_4BiCl_3$•2 C_5H_5N (**2**): 0.154 g (0.488 mmol) of $BiCl_3$ and 0.1 g (0.4 mmol) of 7,10-dioxa-3,14-diazabicyclo[14.3.1]icosa-1(20),16,18-triene-2,15-dione [5] were dissolved in 2.5 mL of pyridine to give a pink-orange solution. This was left to stir at room temperature. After three days, a white solid suspension was separated by filtration and the remaining pale orange solution was stored overnight at −35 °C. Colourless plates suitable for examination by X-ray diffraction formed.

X–Ray Experimental

Crystals of **1** and **2** were mounted on low temperature diffraction loops and measured on a Rigaku Saturn CCD area detector with graphite monochromated Mo–Kα radiation. Structures were solved by direct methods (SHELXS)[6] and expanded using Fourier techniques.[7] Neutral atom scattering factors were taken from Cromer and Waber.[8] Anomalous dispersion effects were included in Fcalc [9]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[10] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[11] All calculations were performed using the OLEX2[12] and PLATON[13] crystallographic software packages, except for refinement, which was performed using SHELXL–2013.[6] Non–hydrogen atoms were refined anisotropically, while hydrogen atoms were introduced in calculated positions and refined on a riding model. For **1** and **2**, anisotropic displacement similarity restraints were applied to some of the bonded atoms in the pyridine rings, while for **2**, isotropic displacement restraints were also applied to several of these atoms. **2** crystallized as a racemic twin in a non-centrosymmetric space group with Flack x = 0.489(5), Hooft y = 0.487(3) and Bayesian statistics which gave P2(True) = n/a, P3(True) = 0, P3(rac-twin) = 1.000, P3(False) = 0.[13] A summary of the X–ray crystallographic data can be found in Table 1.

Structural Descriptions

Trichlorotetrapyridylbismuth(III), $(C_5H_5N)_4BiCl_3$ (**1**), crystallized in $P2_1/n$ with one chemical formula moiety contained in the asymmetric unit (Z' = 1; Figure 1). Bi–L (L = Cl and $N_{pyridine}$) distances and angles are given in Table 2. The geometry about the central Bi is distorted pentagonal bipyramidal. The seven-coordinate nature of this complex is consistent with the report by Norman [3], however, the crystal system in that report was orthorhombic, and no structural details could be included due to pyridine disorder.

Chloride ligands occupy the axial sites, while the equatorial sites are occupied by four $N_{pyridine}$-ligands and a third chloride. Ideal geometry should exhibit equatorial angles of 72 ° and axial angles of 180 °, however, significant deviations can be seen particularly in the equatorial Cl1-Bi-N angles, suggesting that electron density at the chloride repels the pyridine rings. The approximate T-shape geometry that the chloride ligands adopt about the Bi centre is uncommon, with only six structurally documented examples[14] in the Cambridge Structural Database[15] (CSD; *v*. 5.34 with May 2013 update), and no examples where pyridine occupies the remaining coordination sites. Bi^{3+} has a similar ionic radii to La^{3+}, (1.03 Å vs. 1.032 Å)[16] and the analogous pentagonal bipyramidal $(py)_4MCl_3$ coordination geometry has been previously reported for a series of lanthanide (Ln) hemisolvate (py) complexes (Ln = La, Er,[17] Eu[18] and Yb[19]). That isostructural series crystallized in $P2_1/n$ with slightly larger b-axes and β-angles than those reported herein. The resulting cells of larger volume are sensibly associated with the presence of a one-half occupancy pyridine molecule as lattice solvent in the asymmetric unit. Another significant difference between the Ln series and **1** can be found *via* comparison of the dihedral angles between the equatorial N_4Cl plane to the coordinated C_5N ring planes. For the Yb analogue,[19] these were reported as 65.6, 73.2, 87.0, 56.9(1)°, but for **1**, these are 110.6(4), 111.8(6), 111.1(6), 101.0(4) °. For the Ln structures, this skewness from one pyridine ring to another did not result in any π-π interactions in the extended packing motif (though some C_{sp2}-H$\cdots\pi$ interactions were present.) In the case of **1**, however, the near planar arrangement of the pyridine rings lead to both intra- and intermolecular π-π interactions for the pyridine rings that were non-adjacent to the equatorial Cl ligand (Figure 2, Table 3), consistent with the geometries described by Janiak[20] for coordinated heteroaromatic systems, with centroid separations of less than 3.8 Å, and off-set angles of less than 20^{o}. The intramolecular centroid separation of 3.537(13) Å between the pyridines containing N2 and N3 was significantly shorter than the intermolecular separation of 3.823(18) Å, measured for the pyridine containing N3 and its symmetry equivalent, generated by the operation $1 - x$, $1 - y$, $1 - z$. This alignment was accommodated by the presence of two long Bi-N bonds (2.751(13) and 2.816(14) Å), both present for the pyridine rings involved in π-π interactions. A search in the CSD for other Bi-$N_{aromatic}$ bonds yielded 445 observations with an average bond length of 2.58(13) Å, an upper-quartile defined by distances longer than 2.668 Å, and the longest, non-outlier, distance of 2.926 Å.[21] Other weak intermolecular hydrogen-halogen (C_{sp2}-H$\cdots$Cl) interactions were present, which lead to the formation of chains (graph set notation $C^{1}_{1}(5)$) parallel to the b-axis (Figure 3, Table 4).

Trichlorotetrapyridylbismuth(III) pyridine disolvate, $(C_5H_5N)_4BiCl_3$•$2C_5H_5N$ (**2**), crystallized in *P2₁* with four chemical formula moieties (one bismuth complex and two lattice solvent pyridine molecules) contained in the asymmetric unit (Z' = 4; Figure 4). Bi–L (L = Cl and $N_{pyridine}$) distances and angles are given in Table 5. As in **1**, the geometry about each of the central bisumuths is distorted pentagonal bipyramidal. Chloride ligands occupy the axial sites, while the equatorial sites are occupied by four $N_{pyridine}$ ligands and a third chloride. A large number of weak intermolecular hydrogen-halogen (C_{sp2}-H···Cl) interactions were present (Figure 4, Supplementary Table S1). Overlay of each of the Bi complexes in the asymmetric unit yielded a root mean square deviation for Bi2 to Bi1 of 0.592 Å (with inversion), 0.136 Å for Bi4 to Bi1 (with inversion) and 0.588 Å for Bi3 to Bi1 (without inversion; the opposite inversion functions yielded higher RMSDs of 0.625 Å, 0.746 Å and 0.725 Å, respectively.)

2 crystallized in a non-centrosymmetric space group with Flack x = 0.489(5), Hooft y = 0.487(3) and Bayesian statistics which gave P2(True) = n/a, P3(True) = 0, P3(rac-twin) = 1.000, P3(False) = 0. The Flack x, Hooft y values, and the Bayesian statistics are consistent with the fragment match result, which indicates that **2** is a racemic twin.[22] Comparison of the dihedral angles between the equatorial N_4Cl plane to the coordinated C_5N ring planes for the complexes containing Bi1, Bi2, Bi3 and Bi4 are {86.3(6), 76.3(6), 86.8(6), 125.9(6) ^{o}}, {79.0(8), 71.4(6), 74.4(6), 71.4(5) ^{o}}, {68.5(6), 72.4(6), 72.0(5), 89.0(7) ^{o}} and {126.5(6), 92.4(6), 79.0(6), 84.4(6) ^{o}}, respectively. In each case the dihedral angles are similar to those reported for the Yb analogue,[19] and the only π-π interaction observed was an intermolecular interaction between the rings containing

[C16 C17 C18 C19 C7 N4] and [C61 C62 C63 C64 C65 N13], with a centroid-centroid separation of 3.613(11) Å and an angle between the ring planes of 1.9(10) ^{o} (Table 6).

Conclusions

$(C_5H_5N)_4BiCl_3$ and its pyridine solvate have been reported here, which both possess distorted pentagonal bipyramidal coordination geometry. While π-π stacking interactions were observed for **1**, this was not the case in **2**. The presence of lattice solvent pyridine molecules in **2** resulted in many more C-H···Cl interactions than were observed for **1**. Attempts to coordinate $BiCl_3$ with 7,10-dioxa-3,14-diazabicyclo[14.3.1]icosa-1(20),16,18-triene-2,15-dione in pyridine yielded **2**, and not a metallated macrocyclic complex. This result is consistent with the 'soft' nature of Bi^{3+} ions and relative softness of *N*- and π-donors compared with ethereal *O*-atoms.

Acknowledgments

We would like to thank NSERC and the Office of the Dean of Science, Memorial University, for financial support. Hisham Sleem and Dr. Paris Georghiou of Memorial University's Department of Chemistry, are thanked for providing the 7,10-dioxa-3,14-diazabicyclo[14.3.1]icosa-1(20),16,18-triene-2,15-dione used in this study.

References

[1] Gaspard-Iloughmane, H., Le Roux, C. (2004) *Eur. J. Org. Chem.*, 2517-2532.

[2] Nyburg, S. C., Ozin, G.A., Szymanski, J.T. (1971) *Acta Cryst.*, B27: 2298-2304.

[3] James, S.C., Norman, N.C., Orpen, A.G. (1999*) J. Chem. Soc., Dalton Trans*., 2837-2843.

[4] a) {12-crown-4} Alcock, N.W., Ravindran, M., Willey, G.R. (1989) *Chem. Commun*., 1063-1065; b) {15-Crown-5, Benzo-15-crown-5 and 18-Crown-6} Rogers, R. D., Bond, A.H., Aguinaga, S., Reyes, A. (1992) *J. Am .Chem. Soc*., 114: 2967-2977; c) {1,4,7-trioxa-10,13-dithiacyclopentadec-11-ene-11,12-dicarbonitrile and 1,4,7,10-tetraoxa-13,16-dithiacyclo-octadec-14-ene-14,15- dicarbonitrile} Drexler, H.-J., Starke, I., Grotjahn, M., Reinke, H., Kleinpeter, E., Holdt, H.-J. (1999) *Z. Naturforsch., B: Chem. Sci*., 54: 799-806; d) {5,11,17,23,29,35,41,47-octa-t-butyl-49,50,51,52,53,54,55,56-octaoxycalix(8)arene} Liu, L., Zakharov, L.N., Golen, J.A., Rheingold, A.L., Hanna, T.A. (2008) *Inorg .Chem*., 47: 11143-11153; e) {1,4,7,10,13,16-hexaoxacyclo-octadecane} Drew, M.G.B., Nicholson, D.G., Sylte, I., Vasudevan, A. (1990) *Inorg. Chim. Acta*, 171: 11-15; f) {Dibenzo-24-crown-8} Willey, G.R., Aris, D.R., Errington, W. (2000) *Inorg. Chim. Acta*, 300: 1004-1007.

[5] Sleem, H.F., Dawe, L.N., Georghiou, P.E. (2012) *New J. Chem.*, 36: 2451-2455.

[6] Sheldrick, G.M. (2008) *Acta Cryst*., A64: 112-122.

[7] Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R., Smits, J.M.M. (1999) The DIRDIF–99 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

[8] Cromer, D.T., Waber, J.T. (1974) International Tables for X–ray Crystallography, Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A.

[9] Ibers, J.A., Hamilton, W.C. (1964) *Acta Cryst.*, 17: 781-782.

[10] Creagh, D.C., McAuley, W.J. (1992) International Tables for Crystallography, Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pp 219–222.

[11] Creagh, D.C., McAuley, W.J. (1992) International Tables for Crystallography, Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pp. 200–206.

[12] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2009) *J. Appl. Cryst.* 42: 339-341.

[13] Spek, A.L. (2003) *J. Appl. Cryst.*, 36: 7-13.

[14] a) Drew, M.G.B., Kisenyi, J.M., Willey, G.R., (1984) *J. Chem. Soc., Dalton Trans.*, 1723-1726; b) Eveland, J.R., Whitmire, K.H. (1996) *Inorg. Chim. Acta*, 249: 41-46; c) Bowmaker, G.A., Junk, P.C., Lee, A.M., Skelton, B.W., White, A.H. (1998) *Aust. J. Chem.*, 51: 317-324; d) Bowmaker, G.A., Hannaway, F.M.M., Junk, P.C., Lee, A.M., Skelton, B.W., White, A.H. (1998) *Aust. J. Chem.*, 51: 325-330; e) Bowmaker, G.A., Hannaway, F.M.M., Junk, P.C., Lee, A.M., Skelton, B.W., White, A.H. (1998) *Aust. J. Chem.*, 51: 331-336; f) Kyriakidis, C.E., Khristidis, P.C., Rentzeperis, P.J., Tossidis, I.A., Bolos, C.A. (1990) *Z. Kristallogr*. 193: 101-110.

[15] Allen, F.H. (2002) *Acta Cryst.*, B58: 380-388.

[16] Shanno, R. D. (1976) *Acta Cryst.*, A32: 751767.

[17] Li, J.-S., Neumuller, B., Dehnicke, K. (2002) *Z. Anorg. Allg. Chem.*, 628: 45-50.

[18] Hu, N., Lin, Y., Shen, Q., Xing, Y., Shi, E. (1986) *Acta Chim. Sin* (*Huaxue Xuebao),* 44: 388.

[19] Deacon, G.B., Scott, N.M., Skelton, B.W., White, A.H. (2006) *Z. Anorg. Allg. Chem.,* 632: 1945-1946.

[20] Janiak, C. (2000) *Dalton Trans*., 3885-3896.

[21] Anderson, K.M., Baylies, C.J., Jahan, A.H.M.M., Norman, N.C., Orpen, A.G., Starbuck, J. (2003) *Dalton Trans*., 3270-3277.

[22] Hooft, R.W.W., Straver, L.H., Spek, A.L. (2008) *J. Appl. Cryst.,* 41: 96-103.

Figures

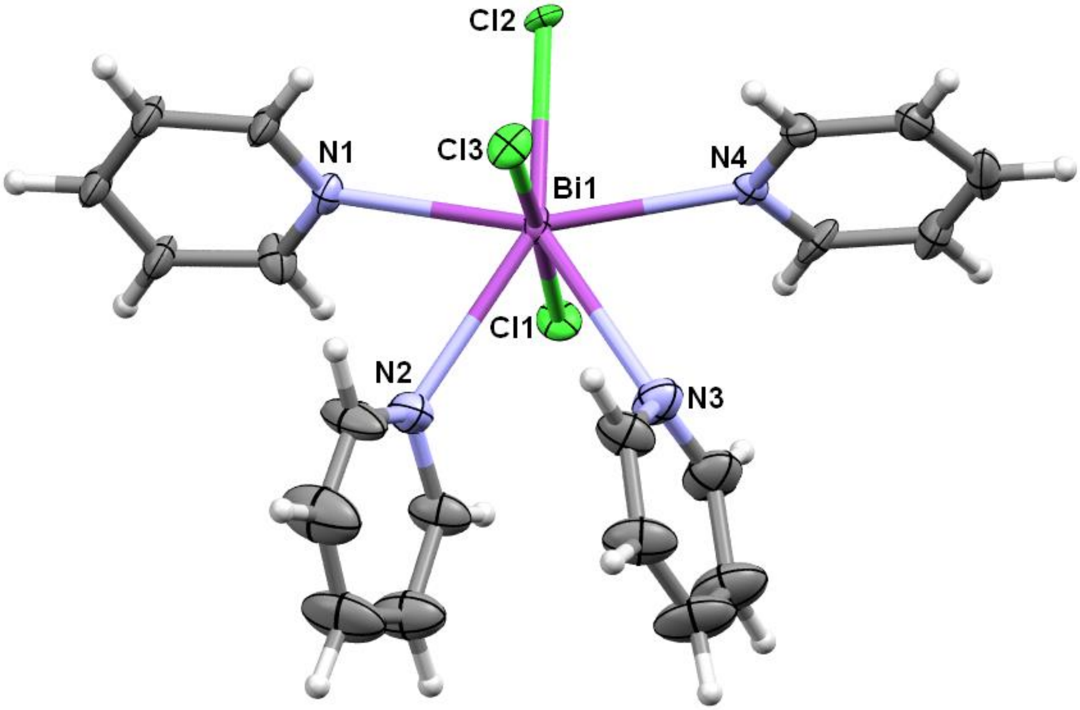

Figure 1: Asymmetric unit of **1**, represented with 50% probability ellipsoids. Labels for C (grey) and H (light grey spheres of arbitrary size) omitted for clarity.

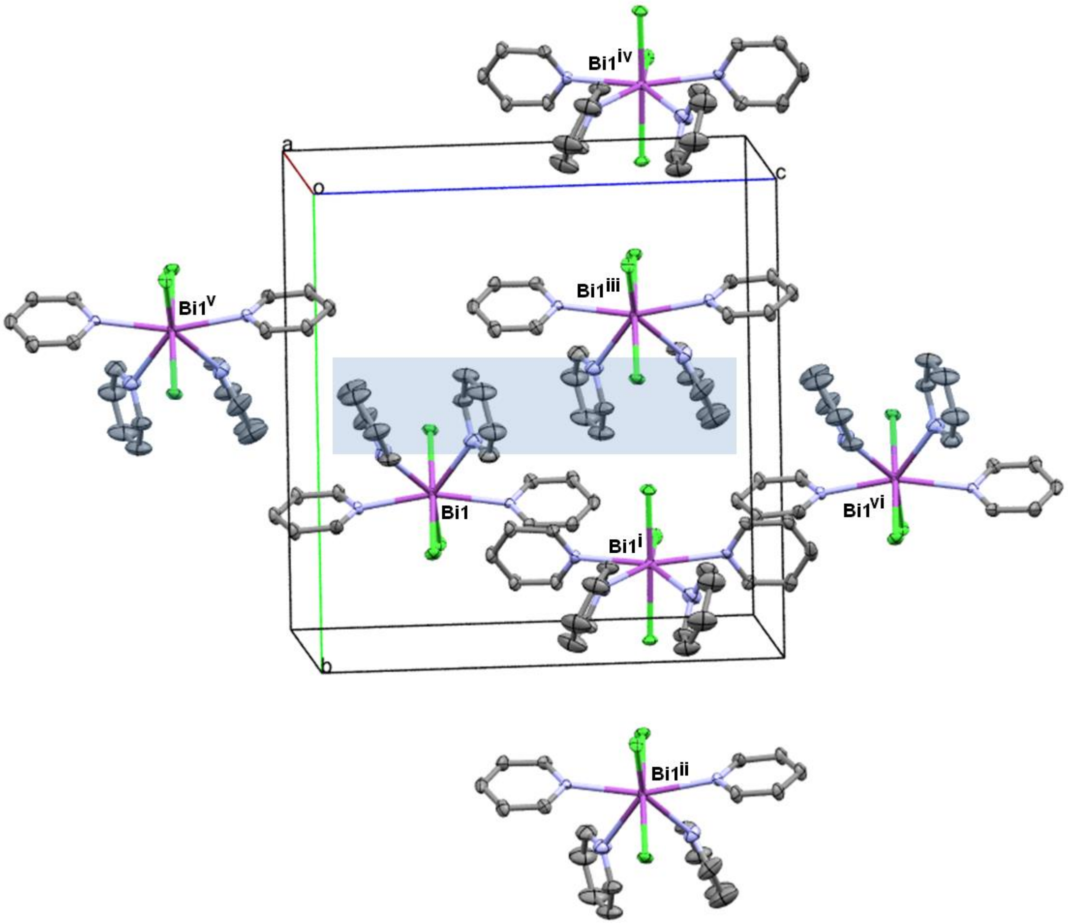

Figure 2: Partially packed unit cell for **1**, with π-π interactions highlighted, represented with 50% probability ellipsoids and with H-atoms omitted for clarity. Symmetry operations: (i) ½ + x, 1.5 – y, ½ + z; (ii) 1 – x, 2 – y, 1 – z; (iii) 1 – x, 1 – y, 1 – z; (iv) ½ + x, ½ – y, ½ + z; (v) 1 – x, 1 – y, – z; (vi) x, y, 1 + z.

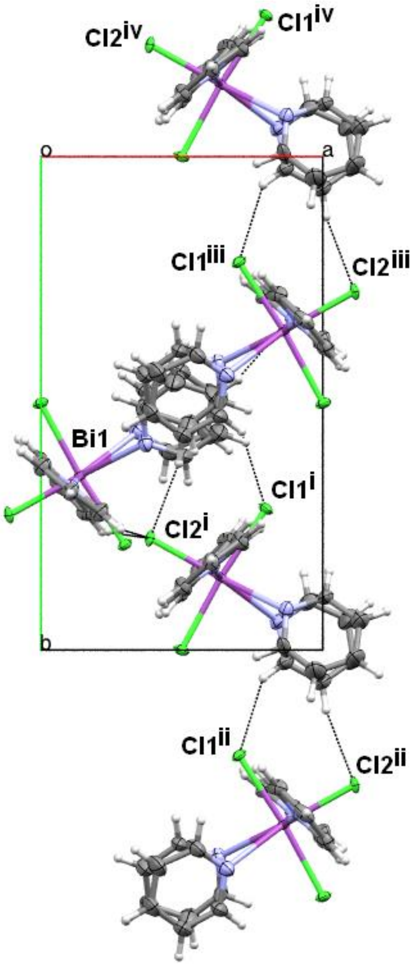

Figure 3: Partially packed unit cell for **1**. View in Figure 2 rotated about the y-axis showing, C-H···Cl interactions, represented with 50% probability ellipsoids and with H-atoms omitted for clarity. Symmetry operations: (i) ½ + *x*, 1.5 – *y*, ½ + *z*; (ii) 1 – *x*, 2 – *y*, 1 – *z*; (iii) 1 – *x*, 1 – *y*, 1 – *z*; (iv) ½ + *x*, ½ – *y*, ½ + *z*; (v) 1 – *x*, 1 – *y*, – *z*; (vi) *x*, *y*, 1 + *z*.

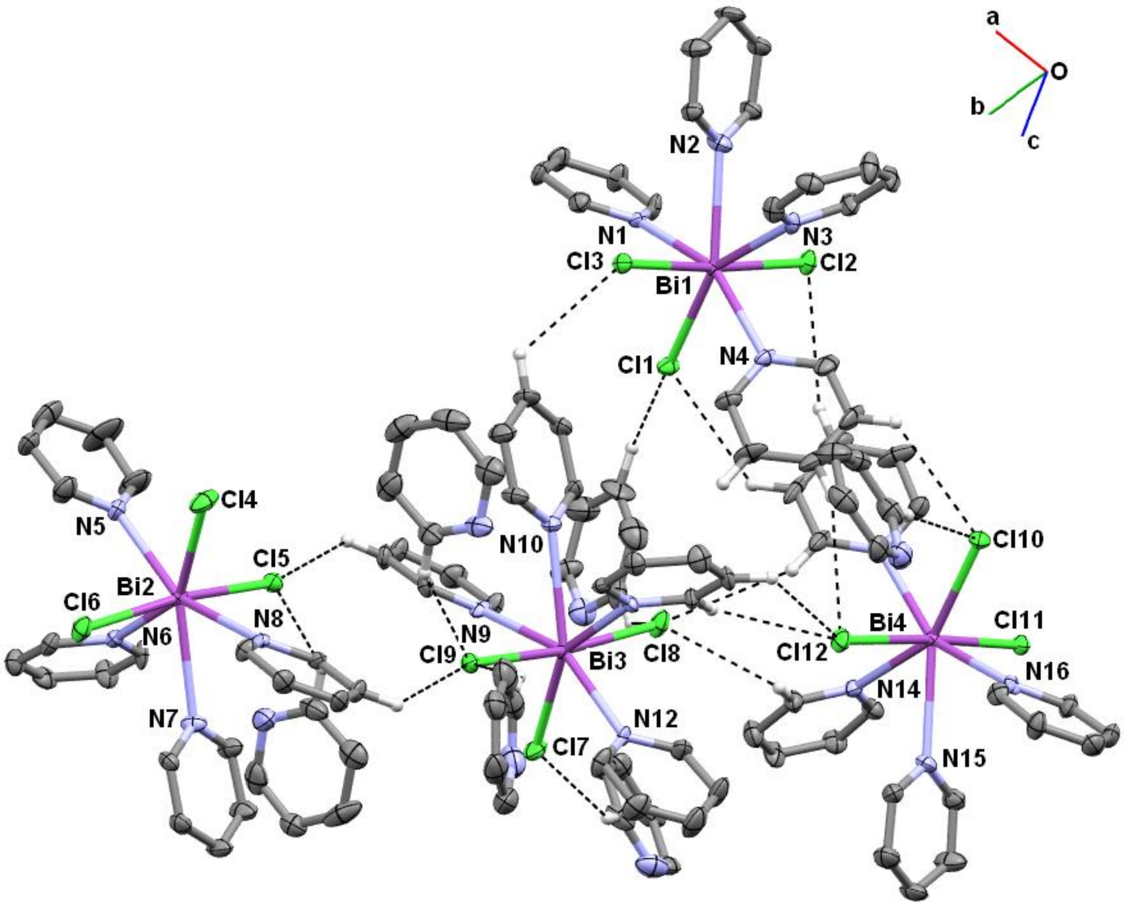

Figure 4: Asymmetric unit of **2**, showing some C-H···Cl interactions, represented with 30% probability ellipsoids. Labels for C (grey), non-coordinated N (blue) and H (light grey spheres of arbitrary size) omitted for clarity. Two lattice solvent pyridine molecules that are not involved in any significant intermolecular interactions were also omitted for clarity.

Tables

Table 1 Summary of Crystallographic Data

Complex	**1**	**2**
Chemical formula	$(C_5H_5N)_4BiCl_3$	$(C_5H_5N)_4BiCl_3$•2 C_5H_5N
Formula Mass	631.73	789.93
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (#14)	$P2_1$ (#4)
a/Å	9.079(4)	16.3898(11)
b/Å	15.949(8)	21.2049(14)
c/Å	15.285(8)	19.2625(14)
α/°	90.00	90.00
β/°	90.807(13)	105.370(7)
γ/°	90.00	90.00
Unit cell volume/Å^3	2213.1(18)	6455.1(8)
Temperature/K	163(2)	123(2)
Z	4	8
Reflections (Total/Unique/I>2σI)	7451/ 4195/ 3676	42948/ 26586/ 22179
R_{int}	0.0667	0.0573
R_1 ($I > 2\sigma(I)$)	0.0745	0.0615
$wR(F^2)$ (all data)	0.1764	0.1527
Goodness of fit on F^2	1.121	1.058
CCDC number	948423	948424

Table 2 Bi-Ligand Lengths (Å) and Angles (^{o}) in **1**

Bi1–Cl1	2.656(3)	Cl2–Bi1–Cl3	90.66(12)
Bi1–Cl2	2.611(3)	Cl2–Bi1–Cl1	94.05(11)
Bi1–Cl3	2.668(3)	Cl1–Bi1–Cl3	175.18(11)
Bi1–N1	2.539(12)	Cl1–Bi1–N2	85.8(3)
Bi1–N2	2.751(13)	Cl2–Bi1–N2	148.7(3)
Bi1–N3	2.816(14)	Cl3–Bi1–N2	89.6(3)
Bi1–N4	2.551(12)	N1–Bi1–Cl1	89.5(3)
		N1–Bi1–Cl2	80.1(3)
		N1–Bi1–Cl3	90.4(3)
		N3–Bi1–Cl1	92.1(3)
		N3–Bi1–Cl1	84.6(3)
		N4–Bi1–Cl1	86.8(3)
		N4–Bi1–Cl2	78.5(3)
		N4–Bi1–Cl3	95.1(3)
		N1–Bi1–N2	68.6(4)
		N1–Bi1–N4	158.0(4)
		N3–Bi1–N4	69.0(4)
		N3–Bi1–N2	64.6(4)
		N4–Bi1–N2	132.6(4)

Table 3 π– π Interactions in **1**

π–π	Centroid–Centroid (Å)	Plane–Plane (Å)	Angle between Planes (°)
Cg2–Cg3	3.537(13)	-3.243(16)	19.1(7)
Cg3–Cg3^{iii}	3.823(18)	-3.39(3)	0.000(12)

Plane–Plane separations measured as the shortest distance from centroid of one pyridine ring to the other plane
Symmetry code: (iii) 1 – *x*, 1 – *y*, 1 – *z*
Cg2 = Centroid of C6 C7 C8 C9 C10 N2
Cg3 = Centroid of C11 C12 C13 C14 C15 N3

Table 4 C–H...Cl Interactions in **1**

Donor	H	Acceptor	D···A (Å)	D–H (Å)	H···A (Å)	D–H···A (°)
C11	H11	Cl1^{vii}	3.701(18)	0.95	2.88	145.5
C12	H12	Cl2^{vii}	3.86(2)	0.95	2.94	163.0

Symmetry code: (vii) = ½ – *x*, ½ – *y*, ½ – *z*

Table 5 Selected Bi-Ligand Lengths (Å) and Angles (°) in **2**

Bi1–Cl1	2.659(5)	Cl1–Bi1–Cl3	94.07(15)
Bi1–Cl2	2.658(5)	Cl2–Bi1–Cl1	90.75(17)
Bi1–Cl3	2.696(4)	Cl2–Bi1–Cl3	175.12(15)
Bi1–N1	2.570(15)	Cl1–Bi1–N2	145.0(4)
Bi1–N2	2.686(15)	Cl1–Bi1–N3	147.3(4)
Bi1–N3	2.703(16)	Cl2–Bi1–N2	85.9(4)
Bi1–N4	2.602(15)	Cl2–Bi1–N3	88.0(4)
		Cl3–Bi1–N3	88.3(4)
		N1–Bi1–Cl1	77.0(3)
		N1–Bi1–Cl2	92.8(4)
		N1–Bi1–Cl3	87.6(4)
		N2–Bi1–Cl3	89.8(4)
		N4–Bi1–Cl1	78.2(4)
		N4–Bi1–Cl2	92.2(4)
		N4–Bi1–Cl3	89.5(4)
		N1–Bi1–N2	68.5(5)
		N1–Bi1–N3	135.7(5)
		N1–Bi1–N4	154.7(5)
		N2–Bi1–N3	67.5(5)
		N4–Bi1– N2	136.7(5)
		N4–Bi1–N3	69.2(5)
Bi2–Cl4	2.641(6)	Cl4–Bi2–Cl5	97.41(19)
Bi2–Cl5	2.692(5)	Cl4–Bi2–Cl6	91.8(2)
Bi2–Cl6	2.664(5)	Cl6–Bi2–Cl5	170.75(17)
Bi2–N5	2.564(15)	Cl4–Bi2–N7	143.3(4)

Table 5 continued… Selected Bi-Ligand Lengths (Å) and Angles (^{o}) in **2**

Bi2–N6	2.680(16)	Cl4–Bi2–N6	145.7(3)
Bi2–N7	2.740(14)	Cl5–Bi2–N7	88.9(4)
Bi2–N8	2.573(14)	Cl6–Bi2–N6	87.1(4)
		Cl6–Bi2–N7	83.4(4)
		N5–Bi2–Cl4	77.2(4)
		N5–Bi2–Cl5	91.7(4)
		N5–Bi2–Cl6	90.6(4)
		N6–Bi2–Cl5	85.5(4)
		N8–Bi2–Cl4	76.7(3)
		N8–Bi2–Cl5	86.3(3)
		N8–Bi2–Cl6	95.5(3)
		N5–Bi2–N6	68.5(5)
		N5–Bi2–N7	138.9(5)
		N5–Bi2–N8	153.4(5)
		N6–Bi2–N7	70.7(5)
		N8–Bi2–N6	137.6(4)
		N8–Bi2–N7	67.6(5)
Bi3–Cl7	2.664(5)	Cl7–Bi3–Cl8	91.35(19)
Bi3–Cl8	2.675(5)	Cl7–Bi3–Cl9	95.88(17)
Bi3–Cl9	2.681(5)	Cl8–Bi3–Cl9	172.67(18)
Bi3–N9	2.573(15)	Cl7–Bi3–N10	142.9(4)
Bi3–N10	2.738(14)	Cl7–Bi3–N11	147.1(3)
Bi3–N11	2.690(15)	Cl8–Bi3–N10	83.2(4)
Bi3–N12	2.546(14)	Cl8–Bi3–N11	87.7(3)
		Cl9–Bi3–N10	90.3(3)
		Cl9–Bi3–N11	86.9(3)
		N9–Bi3–Cl7	77.2(3)
		N9–Bi3–Cl8	95.7(4)
		N9–Bi3–Cl9	84.8(4)
		N12–Bi3–Cl7	77.8(4)
		N12–Bi3–Cl8	92.1(4)
		N12–Bi3–Cl9	90.6(4)
		N9–Bi3–N10	67.0(5)
		N9–Bi3–N11	135.7(5)
		N11–Bi3–N10	69.6(5)
		N12–Bi3–N9	154.0(5)
		N12–Bi3–N10	138.8(5)
		N12–Bi3–N11	69.3(5)
Bi4–Cl10	2.638(5)	Cl10–Bi4–Cl11	93.87(15)
Bi4–Cl11	2.697(4)	Cl10–Bi4–Cl12	90.20(16)
Bi4–Cl12	2.661(5)	Cl12–Bi4–Cl11	175.92(16)
Bi4–N13	2.613(16)	Cl10–Bi4–N15	143.6(4)

Table 5 continued… Selected Bi-Ligand Lengths (Å) and Angles (^{o}) in **2**

Bi4–N14	2.666(16)	Cl10–Bi4–N14	149.2(3)
Bi4–N15	2.689(15)	Cl12–Bi4–N14	88.2(4)
Bi4–N16	2.587(15)	Cl12–Bi4–N15	85.5(4
		N13–Bi4–Cl10	78.5(4)
		N13–Bi4–Cl11	87.9(4)
		N13–Bi4–Cl12	92.7(4)
		N14–Bi4–Cl11	88.2(4)
		N15–Bi4–Cl11	91.3(4)
		N16–Bi4–Cl10	76.8(3)
		N16–Bi4–Cl11	87.1(4)
		N16–Bi4–Cl12	94.0(4)
		N13–Bi4–N14	70.8(5)
		N13–Bi4–N15	137.8(5)
		N14–Bi4–N15	66.9(5)
		N16–Bi4–N13	154.4(5)
		N16–Bi4–N14	134.0(4)
		N16–Bi4–N15	67.5(5)

Table 6 π– π Interactions in **2**

π–π	Centroid–Centroid (Å)	Plane–Plane (Å)	Angle between Planes (^{o})
Cg4 Cg13	3.613(11)	3.304(17)	1.9(10)

Plane–Plane separations measured as the shortest distance from centroid of one pyridine ring to the other plane
Cg4 = Centroid of C16 C17 C18 C19 C7 N4
Cg13 = Centroid of C61 C62 C63 C64 C65 N13

Supplementary Materials

Table S1 C–H···Cl Interactions in **2**

Donor	H	Acceptor	D···A (Å)	D–H (Å)	H···A (Å)	D–H···A (°)
C49	H49	Cl1	3.86(2)	0.95	2.97	155.4
C64	H64	Cl1	3.84(2)	0.95	3.14	132.2
C88	H88	Cl1	3.58(3)	0.95	2.82	137.4
C5	H5	Cl2	3.72(2)	0.95	2.99	134.3
C15	H15	Cl2	3.60(3)	0.95	2.87	133.6
C1	H1	Cl3	3.52(2)	0.95	2.80	133.8
C11	H11	Cl3	3.69(2)	0.95	2.97	134.2
C6	H6	Cl3	3.70(2)	0.95	2.97	134.0
C93	H93	Cl3^{i}	3.84(3)	0.95	3.01	147.1
C79	H79	Cl3^{ii}	3.69(2)	0.95	2.97	134.3
C86	H86	Cl3^{i}	3.77(3)	0.95	3.04	135.1
C110	H110	Cl4^{ii}	3.67(3)	0.95	2.89	140.5
C58	H58	Cl4^{ii}	3.92(3)	0.95	3.07	149.0
C40	H40	Cl5	3.51(2)	0.95	2.81	131.7
C35	H35	Cl5	3.74(2)	0.95	3.05	130.8
C105	H105	Cl5	3.84(3)	0.95	3.09	136.5
C25	H25	Cl5	3.69(3)	0.95	2.97	133.6
C73	H73	Cl5^{ii}	3.659(19)	0.95	2.75	160.4
C31	H31	Cl6	3.51(2)	0.95	2.81	131.5
C97	H97	Cl6^{iii}	3.75(3)	0.95	3.01	136.1
C16	H16	Cl6^{iv}	3.92(3)	0.95	3.07	148.8
C21	H21	Cl6	3.65(2)	0.95	2.96	130.1
C23	H23	Cl7^{v}	3.74(3)	0.95	2.84	158.4
C117	H117	Cl7^{vi}	3.77(3)	0.95	2.87	159.7
C55	H55	Cl8	3.64(2)	0.95	2.95	130.6
C50	H50	Cl8	3.48(2)	0.95	2.79	130.5
C56	H56	Cl8	3.65(2)	0.95	2.93	132.8
C90	H90	Cl8	3.78(3)	0.95	3.03	136.1
C51	H51	Cl9	3.59(2)	0.95	2.90	130.8
C41	H41	Cl9	3.49(2)	0.95	2.80	130.2
C8	H8	Cl9^{vii}	3.66(2)	0.95	2.78	154.3
C60	H60	Cl9	3.59(2)	0.95	2.86	134.8
C111	H111	Cl9	3.71(2)	0.95	2.89	145.6
C120	H120	Cl9	3.88(4)	0.95	3.13	138.0
C32	H32	Cl10^{viii}	3.75(2)	0.95	2.87	154.2
C99	H99	Cl10^{i}	3.54(3)	0.95	2.84	131.4
C17	H17	Cl10	3.82(2)	0.95	3.13	131.1
C81	H81	Cl10	3.99(3)	0.95	3.05	170.5
C2	H2	Cl11^{v}	3.87(2)	0.95	3.15	134.0
C108	H108	Cl11^{ix}	3.77(2)	0.95	3.03	135.8

Table S1 continued... C–H···Cl Interactions in **2**

Donor	H	Acceptor	D···A (Å)	D–H (Å)	H···A (Å)	D–H···A (°)
C80	H80	Cl11	3.54(2)	0.95	2.80	135.1
C70	H70	Cl11	3.65(2)	0.95	2.93	133.2
C85	H85	Cl11^{ix}	3.70(3)	0.95	2.80	158.5
C71	H71	Cl11	3.81(2)	0.95	3.08	134.6
C75	H75	Cl12	3.56(2)	0.95	2.87	130.5
C55	H55	Cl12	3.63(2)	0.95	2.93	131.0
C66	H66	Cl12	3.61(2)	0.95	2.89	133.2
C76	H76	Cl12	3.76(2)	0.95	3.06	132.0
C18	H18	Cl12	3.94(2)	0.95	3.11	146.7
C106	H106	Cl12	3.91(2)	0.95	2.97	170.3

Symmetry code: (i) = -*x*, *y*+1/2, –*z*; (ii) = 1–*x*, *y*, *z*; (iii) = 1–*x*, *y*+1/2, 1–*z*; (iv) = 1–*x*, *y*, 1–*z*; (v) = 1+*x*, *y*, *z*; (vi) = -*x*, *y*–1/2, 1–*z*; (vii) = *x*, *y*, *z*–1; (viii) = 1+*x*, *y*, 1+*z*; (ix) = –*x*–1, *y*–1/2, –*z*.