J Chem Crystallogr (2013) 43:471–477
DOI 10.1007/s10870-013-0445-7

ORIGINAL PAPER

Helical Structures of Tribenzylamine Supramolecular Complexes with $[CoCl_4]^{2-}$/$[CuCl_4]^{2-}$, and Conformational Comparisons of Tribenzylamine in Different Supramolecular Complexes

Hong-yu Guan · Hui-de Shao · Lei Li · Jian-ming Jia · Fang Guo

Received: 6 December 2012 / Accepted: 10 July 2013 / Published online: 26 July 2013

Abstract The compound tribenzylamine (TBA) and its derivatives are a type of classical tripodal ligands in building up diversity of supramolecular arrays or networks. In the present contribution, we described two new supramolecular complexes $2[C_{21}H_{22}N^{+}]\cdot[CoCl_4]^{2-}\cdot$(**1**) and $2[C_{21}H_{22}N^{+}]\cdot[CuCl_4]^{2-}$ (**2**) by reacting protonated TBA with $CoCl_2\cdot 6H_2O$/$CuCl_2\cdot 2H_2O$. Different from previous TBA supramolecular complexes, these two supramolecular complexes were easier to obtain by grinding protonated TBA and $CoCl_2\cdot 6H_2O$/$CuCl_2\cdot 2H_2O$ in an agate mortar than using conventional solution method. The two supramolecular complexes form fascinating 3D helical architectures, with two types of interwoven helical chains involved inside the structures. A comparison of the geometries of TBA in these two supramolecular complexes with the previously reported TBA supramolecular complexes shows that the significant differences are due to the conformation of the three arms of phenyl rings around the N center.

Keywords Tripodal ligand · Tribenzylamine · $[CoCl_4]^{2-}$/$[CuCl_4]^{2-}$ · Helices · Conformation

Introduction

Tripodal ligands are of particular research interest owing to their assembling capacity into the construction of well-defined metal coordination complexes and the potential properties in photoluminescence, magnetism, electronics and catalysis etc [1–7]. Thus, tripodal ligands such as tribenzylamine [8] (TBA) and its derivatives, [9–15] have attracted much attention in building up diversity of supramolecular arrays or networks. The compound TBA, $N(CH_2C_6H_5)_3$, is an aliphatic tertiary amine with bulky substituents, which may exhibit various kinds of conformations, since the molecule has six intramolecular rotation axes. Therefore, taking into account such conformational flexibility, the supramolecular diversity and complexity of H-bonding networks can be further developed by changing the length and flexibility of the three arms of TBA, which could influence the structural and functional properties.

By searching CSD [16], a series of supramolecular complexes of TBA have been reported, including TBA supramolecular complex with carbon tetrabromide solvate $C_{21}H_{21}N\cdot CBr_4$ [17], TBA supramolecular complex by reacting melted TBA with cluster molybdenum dichloride $3(C_{21}H_{22}N^{+})\cdot Cl_{13}Mo_6O_3^{-}$ [18] and TBA supramolecular complex with (μ3-oxo)-heptakis(μ3-chloro)-hexachloro-hexa-molybdenum $C_{21}H_{22}N^{+}\cdot C_{10}HO_{12}Os_3S^{-}$ [19]. In addition, TBA supramolecular complexes with tetrachlorometallates or hexachlorometallates have also been reported, such as $2(C_{21}H_{22}N^{+})\cdot[AuCl_4]^{2-}\cdot Cl^{-}$, [20] 3 $(C_{21}H_{22}N^{+})$ $[PtCl_6]^{2-}\cdot Cl^{-}$ [21]. We also reacted TBA with hexachlorotellurate/hexachlorostannate/hexachlororhennate to successfully produce supramolecular complexes, $[2(C_{21}H_{22}N^{+})\cdot[TeCl_6]^{2-}$ and $[SnCl_6]^{2-}/[ReCl_6]^{2-}]$ [22]. TBA can also form supramolecular complex with tetrachloro-cooper (II)$(C_{21}H_{22}N^{+}\cdot C_{14}H_{16}N^{+}\cdot[CuCl_4]^{2-})$, however the dibenzylammonium was also included in the supramolecular complex [23]. In this article, we have successfully obtained two novel supramolecular complexes with $[CoCl_4]^{2-}$ and $[CuCl_4]^{2-}$, producing $2[C_{21}H_{22}N^{+}]\cdot[CoCl_4]^{2-}$ and $2[C_{21}H_{22}N^{+}]\cdot[CuCl_4]^{2-}$ (**1** and **2**). These two complexes are isostructural and crystallized in orthorhombic system, which are different from the previous reported TBA supramolecular complexes. It is worth

H. Guan · H. Shao · L. Li · J. Jia · F. Guo (✉)
College of Chemistry, Liaoning University,
Shenyang 110036, China
e-mail: fguo@lnu.edu.cn

addressing that the two supramolecular complexes were rendered difficult using conventional solution method, instead, they can be easily obtained by grinding protonated TBA and $CoCl_2 \cdot 6H_2O/CuCl_2 \cdot 2H_2O$ in an agate mortar with a very small amount of ethanol to aid the process. A comparison of the geometries of TBA in these two supramolecular complexes with the previously reported TBA supramolecular complexes [17–23] shows that the significant differences are due to the conformation of the three arms of phenyl rings around the N center.

Experimental

Materials

All starting materials were commercially available, reagent grade, and used without further purification. IR spectra were obtained with a PerkinElmer 100 FT-IR spectrometer using KBr pellets. ^{1}H-NMR spectra were recorded on a Mercury-Plus 300 spectrometer (VARIAN, 300 MHz) at 25 °C with TMS as internal reference.

Preparation of Ligand TBA and its Hydrochloride Crystal $[TBA \cdot H]^+Cl^-$

19 mL dibenzylamine was slowly added to a solution of 17.32 g $NaHCO_3$ and 20 mL distilled water. 16.5 ml benzyl chloride then continuously added into the above mixture solution. After the reaction was heated to 90 °C and stirred for 8 h, the mixture was cooled to room temperature. The reaction product was filtered out, and then washed with distilled water for three times. Recrystallization using anhydrous ethanol and drying in vacuo produced white crystals of TBA 30.74 g, yield 53.55 %. mp 92–93 °C. IR (KBr), λ_{max}/cm^{-1} 3,083, 3,062, 3,026 (w, ArH), 1,602, 1,584, 1,493, 1,452 (s, Ar), 2,923, 2,880 (s, CH_2). ^{1} H NMR ($CDCl_3$, 300 MHz): δ 3.55 (6H, s, CH_2), 2.46 (4H, s, CH_2), 7.22–7.42 (15H, m, ArH). 0.001 mol TBA product, 1 mL concentrated hydrochloric acid and 25 mL ethanol were mixed and dissolved in 50 mL Erlenmeyer flask. The flask was allowed to stand for overnight, giving rise to white and transparent hydrochloride crystals $[TBA \cdot H]^+Cl^-$.

Preparation of Supramolecular Complex of $[2H \cdot 2TBA]^{2+} \cdot [CoCl_4]^{2-}$ (Crystal **1**)

0.72 g TBA, 25 mL ethanol and 0.81 g $CoCl_2 \cdot 6H_2O$ were placed in a 50 mL Erlenmeyer flask, then 1 mL concentrated hydrochloric acid was added and the mixture was shaken until the contents were dissolved. The flask was allowed to stand for about 10 days at room temperature. After the crystals were separated out by filtration, recrystallization with anhydrous ethanol gave rise to blue and transparent block crystals **1**. mp 157–159 °C. IR (KBr), λ_{max}/cm^{-1} 3,010 (w, ArH), 2,955 (s, CH_2), 1,637, 1,498, 1,457 (s, Ar), 2,780, 2,725, 2,609 (w, N^+H). ^{1}H NMR (DMSO, 300 MHz) δ 4.17(12H, s, CH_2), 7.41–7.48 (30H, m, ArH), 10.80 (2H, s, N^+H).

Preparation of Supramolecular Complex of $[2H \cdot 2TBA]^{2+} \cdot [CuCl_4]^{2-}$ (Crystal **2**)

0.56 g TBA, 25 mL ethanol and 0.51 g $CuCl_2 \cdot 2H_2O$ were placed in a 50 mL Erlenmeyer flask, then 1 mL concentrated hydrochloric acid was added and the mixture was shaken until the contents were dissolved. The flask was allowed to stand for about 6–7 days at room temperature. After the crystals were separated out by filtration, recrystallization with anhydrous ethanol gave yellow and transparent block crystals **2**. mp 134.3–136.5 °C. IR (KBr), λ_{max}/cm^{-1} 3,003 (w, ArH), 2,947 (s, CH_2), 1,629, 1,495, 1,454(s, Ar), 2,782, 2,721, 2,604 (w, N^+H). ^{1}H NMR (DMSO, 300 MHz) δ 4.27(12H, s, CH_2), 7.45–7.21 (30H, m, ArH), 11.24 (2H, s, N^+H).

Crystallography

Single-crystal X-ray diffraction measurements of complexes were carried out on a Bruker Smart CCD diffractometer equipped with a graphite monochromator. The determination of unit cell parameters and data collection were performed with Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained with least-squares refinements and the structures were determined using direct methods and refined (based on F^2 using all independent data) by full-matrix least-square methods (SHELXTL 97) [24, 25]. The details of data collection, data reduction, and crystallographic data are summarized in Table 1, and CCDC 913624–913625 contain the supplementary crystallographic data for crystal 1 and 2 in this paper. CCDC 720917 contains the supplementary crystallographic data for the crystal of TBA hydrochloride $[TBA \cdot H]^+Cl^-$.

Powder X-ray diffraction data were recorded at ambient temperature in transmission mode on a Siemens D5000 diffractometer, using Ge monochromated CuK_α radiation ($\lambda = 1.5406$ Å).

Results and Discussion

Synthesis

The formation of two supramolecular complexes of $[2H \cdot 2TBA]^{2+} \cdot [XCl_4]^{2-}$ (X = Co, Cu) was rendered

Table 1 Crystal data and refinement summary for crystal **1** and **2**

Empirical formula	**1** $C_{42}H_{44}Cl_4CoN_2$	**2** $C_{42}H_{44}Cl_4Cu\ N_2$
Formula weight	777.52	782.13
Crystal dimensions (mm)	0.26 × 0.20 × 0.12	0.26 × 0.20 × 0.12
Crystal temperature (K)	113(2)	113(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Z	4	4
a (Å)	10.403(2)	10.228(2)
b (Å)	13.393(3)	13.275(3)
c (Å)	28.013(6)	28.485(6)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	3,902.8(14)	3,867.7(13)
D_x (Mg cm^{-3})	1.323	1.343
μ (mm^{-1})	0.745	0.873
F (000)	1,620	1,628
R_{int}	0.0387	0.0352
No. of total reflns	26,665	28,575
No. of unique reflns	6,871	6,813
No. of data with I > 2σ (I)	6,579	6,499
No. of parameters varied	450	460
s	1.062	1.049
R_f/wR_f	0.0284/0.0635	0.0271/0.0594
All data R_f/wR_f	0.0300/0.0644	0.0292/0.0607

difficult using solution method. We have tried using different solvents (e.g. MeOH, EtOH, DMSO, THF, Acetone et al.) to grow the crystals of supramolecular complexes, thus far, the only one successful crystallization is obtained by slow evaporation from the ethanol, but the outcome is not readily reproducible. Instead, the mechanochemical synthesis [26], where two or more solids react induced by mechanical energy (i.e., external stimuli) such as manual grinding or ball milling, can be readily applied into the preparation of two supramolecular complexes of TBA using liquid assisted grinding [27]. During the preparation of supramolecular complex 1, two components of $[C_{21}H_{22}N]\cdot HCl$ and $CoCl_2\cdot 6H_2O$ in 2:1 molar ratio were ground in an agate mortar for 20 min with 10 μL anhydrous ethanol to aid the process. The comparison between the X-ray powder diffraction measured on the ground polycrystalline product and that calculated on the basis of the structure determined by single crystal X-ray diffraction is shown in Fig. 1. The same experimental operation was carried out for the preparation of complexes **2**, in which the two components of $[C_{21}H_{22}N]\cdot HCl$ and $CuCl_2\cdot 2H_2O$ in 2:1 molar ratio were ground in an agate mortar.

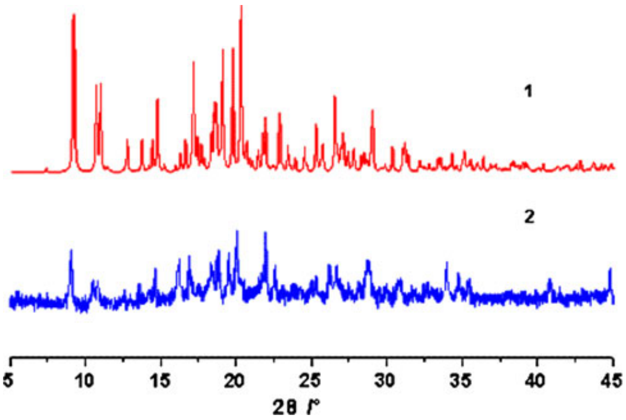

Fig. 1 Comparison of PXRD patterns of supramolecular complex **1** from solution synthesis (*1*) and solid-state synthesis (*2*)

Crystal Structures of **1** and **2**

X-ray crystallography reveals that both structures **1** and **2** are orthorhombic $P2_12_12_1$, with a similar crystal lattice. One asymmetric unit contains one dianion $[CoCl_4]^{2-}$ (in **1**) or $[CuCl_4]^{2-}$ (in **2**) and two protonated independent molecules of **TBA** (Fig. 2). A detailed description will be presented only for **1**, as **2** is similar to **1** except for slight variations in structural and thermal parameters which may be ascertained from the Supplementary material.

The Co atom in **1** has a highly distorted tetrahedral coordination environment from Cl atoms, with the Co–Cl bond lengths in the range of 2.2611(8)–2.2947(7) Å, and Cl–Co–Cl bond angles in the range of 107.01(3)–114.48(3)°. The two independent TBA ligands (labelled L^a and L^b) in one asymmetric unit arrange in a different structural feature. The three benzyl groups are more symmetric in one ligand (labelled L^a) than the other ligand (labelled L^b) (Fig. 3), which can be identified by the distances of centroids of three phenyl rings. In one ligand, the distances are nearly equal with 6.139, 6.312 and 6.397 Å, respectively; while for the other ligand, one benzyl ring is significantly tilted with respect to the other benzyl group, with the distance between the centroid of two benzyl rings is shortened to 4.417 Å, and the other two distances between the centroids of benzyl rings are 5.336 and 7.474 Å, respectively.

The structure of **1** contains a fascinating 3D helical architecture, consisting of two similar types of interwoven helical chains illustrated in Fig. 4. In type I, one period of the helix comprises four ligands and two $[CoCl_4]^{2-}$ anions. The helix is ca. 28.0 Å in pitch. The two independent ligands are assembled into a dimer through C–H···π

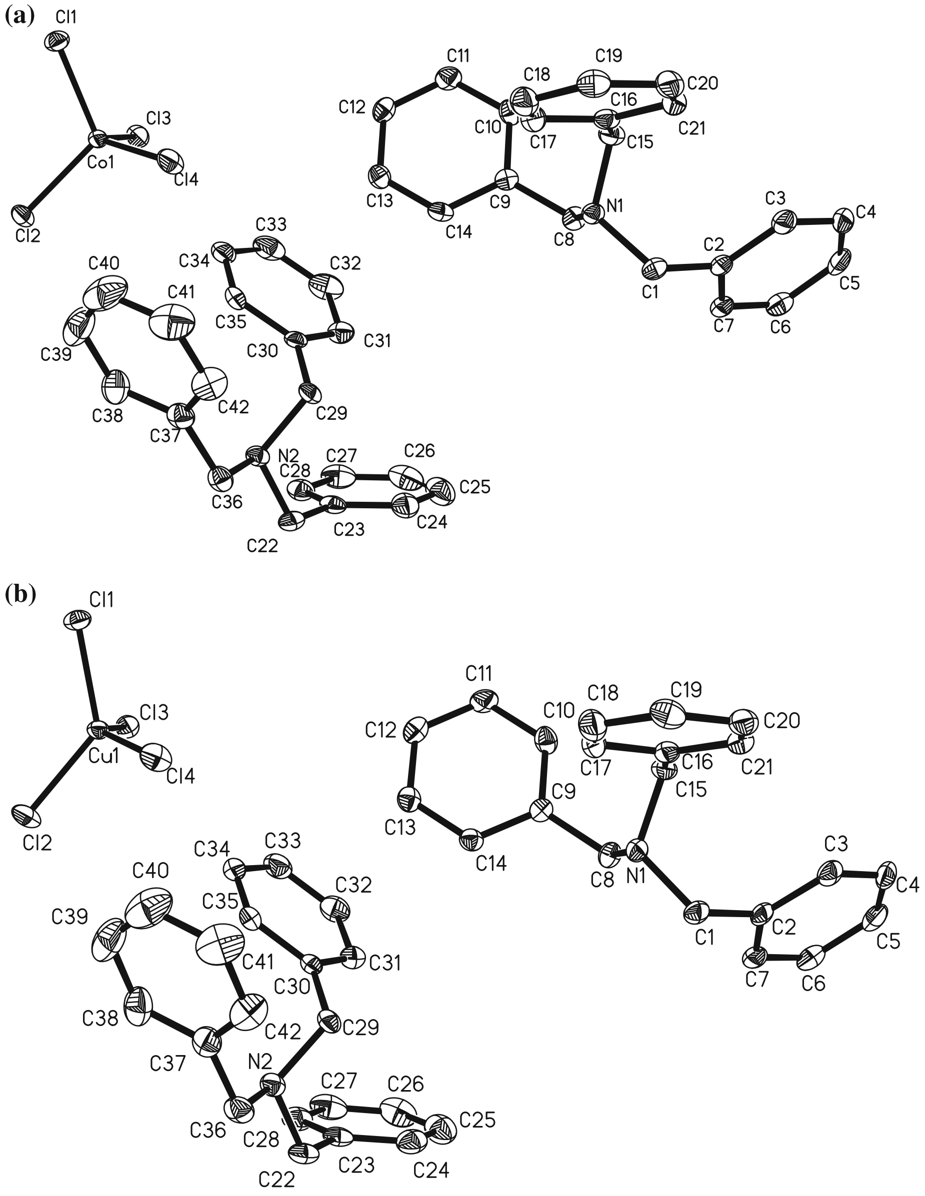

Fig. 2 Crystal structures of supramolecular complex **1** (**a**) and **2** (**b**)

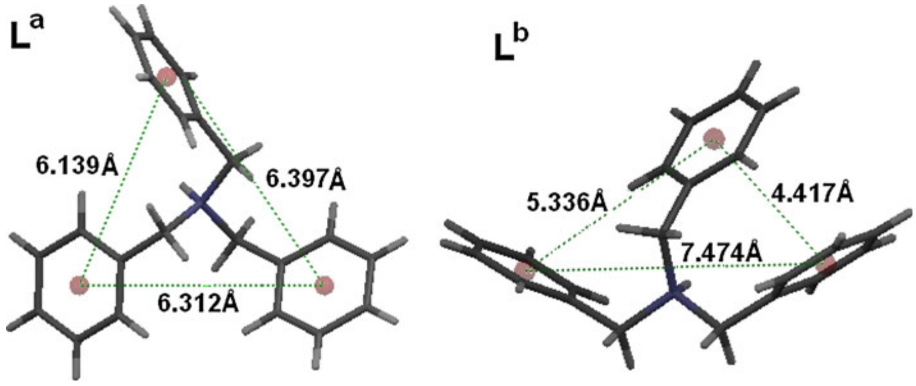

Fig. 3 The conformation comparison of two TBA molecules in one asymmetric unit

interactions ($C13_{phenyl}$–H13···Cg (centroid of phenyl ring [C30–C35] in the other ligand): 3.298 Å, 129.2°). The dimers are further connected with $[CoCl_4]^{2-}$ anions, in which two chloride atoms of $[CoCl_4]^{2-}$ anions acting as acceptors are hydrogen bonded to the adjacent ligand dimers through N–H···Cl interactions

[N2–H2···Cl2 3.244 Å, 162.4°] and C–H···Cl interactions [C11–H11···Cl1 3.620 Å, 147.0°], as seen in Fig. 4a.

The grooves of the helices are mutually occupied by type II of helices. The ligand dimer formed by above C–H···π interactions is also connected with $[CoCl_4]^{2-}$ anions through the other N–H···Cl hydrogen bonding [N1–H1···Cl1 3.241(1) Å, 166.3(1)°] and C–H···Cl interaction [C36–H36···Cl2 3.669 Å, 145.9°], constructing one period of the helix. The periods are further linked into the helical chain along c axis through C–H···π interactions between C20 of phenyl ring [C16–C21] and centroid (Cg) of phenyl ring [C23–C28] (C20–H20···Cg 3.370 Å, 135.3°), as seen in Fig. 4b.

Two types of infinite double helices as well as their interlocking are shown in Fig. 4c.

Comparison of Conformation of TBA

We have concerned with the question about to what extent the conformation of TBA in different compounds is changed from that of pure phase of TBA obtained previously. Bearing this question in mind, we have searched the crystal structures containing TBA component from CSD database [28]. For the convenience of comparison, we have labeled the crystal structures as I (RefCode: TBENZA), II (RefCode: RERCIB), III (RefCode: GINFEO), IV(CCDC number: 720917), V (Refcode: YURQAE), VI (RefCode: YURQEI), VII (RefCode: HATROJ), VIII (RefCode: RERCIB TIPBUQ), IX (RefCode: DUMGIC), respectively.

We have noticed that the conformation of TBA has exhibited great difference due to the protonation of nitrogen atoms in TBA. When the nitrogen atom is not protonated, the distances between centroid of the three benzene rings are nearly equilateral, for example, 6.280 Å/6.334 Å/6.377 Å in TBA (Fig. 5I); 6.143 Å/6.296 Å/6.302 Å in the supramolecular complex of TBA·CBr_4 (Fig. 5II), and 6.140 Å/6.234 Å/6.634 Å in the supramolecular complex with (μ3-oxo)-heptakis(μ3-chloro)-hexa-chloro-hexa-molybdenum (Fig. 5III). After the nitrogen atom is protonated and form supramolecular complex $TBAH^+Cl^-$ (IV), the three distances between the centroid of the benzene rings become completely equilateral with 6.587 Å. This change can be ascribed to the protonated N atoms and its hydrogen bonding with chloride anions, in which the chloride anions as acceptor, are hydrogen bonding with the protonated N atom (N–H···Cl 3.012 Å, 180°) and three methylene groups (3.581 Å, 144.9°) simultaneously.

However, in the supramolecular complex of TBA with chlorometallates, it is noticed that one benzene ring is significantly tilted with respect to the other benzene ring, thus leading to the shortening of the distance between two benzene rings, for example, 3.983 Å/5.893 Å/7.541 Å in the supramolecular complex of $[TBA]H^+{\cdot}0.5[SnCl_6]^{2-}$ (V), 4.030 Å/5.868 Å/7.548 Å in $[TBA]H^+{\cdot}0.5[ReCl_6]^{2-}$ (VI). A similar case occurs in the cocrystal of TBA. Dibenzylamine·$[CuCl_4]^{2-}$ (VII), the distances are 3.851 Å/5.964 Å/7.537 Å respectively. When two or more TBA ligands are involved in one asymmetric unit, it is found that the significant change only occurs in one ligand, for example, in the supramolecular complex of $3[TBAH^+][PtCl_6]^{2-}Cl^-$(VIII), 3.915 Å/6.017 Å/7.556 Å for one ligand, 6.519 Å/6.557 Å/6.666 Å and 6.350 Å/

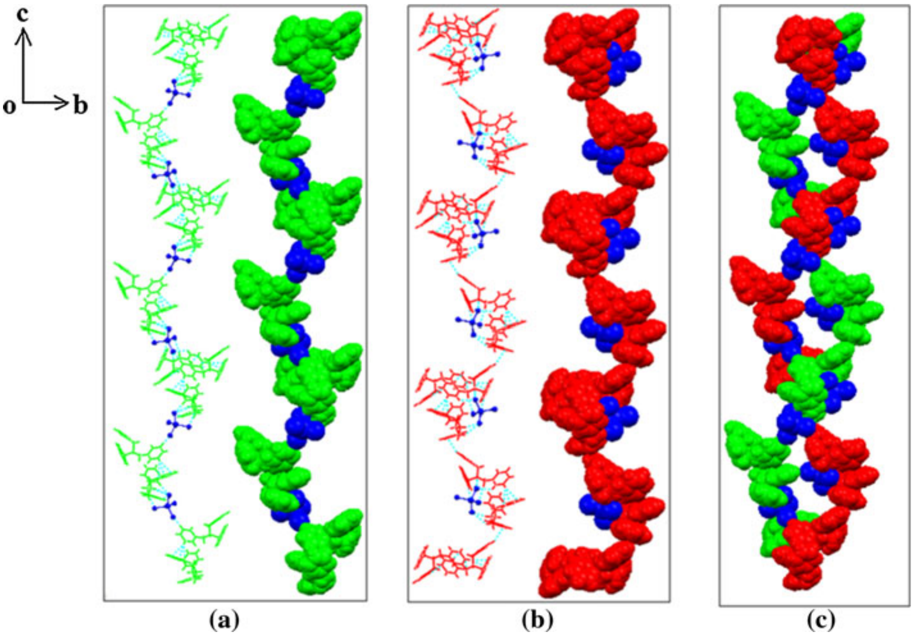

Fig. 4 **a** Type I of helices, **b** Type II of helices, **c** Two types of infinite double helices as well as their interlocking along c axis

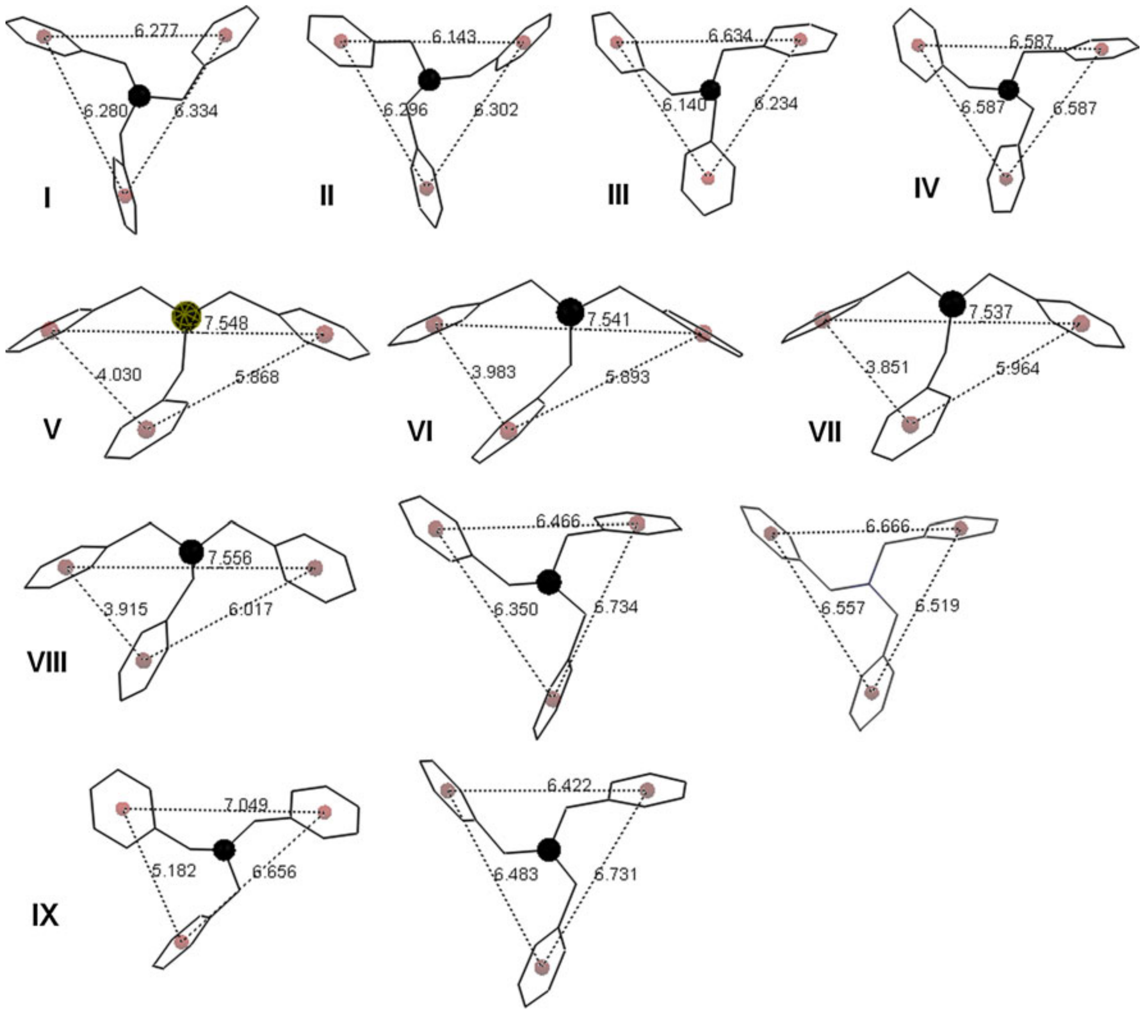

Fig. 5 Conformational comparison of TBA in the reported TBA supramolecular complexes

Table 2 The dihedral angles between benzene rings and the plane formed by three methylene carbon atoms in TBA supramolecular complexes

	I	II	III	IV	V	VI	VII	VIII			IX	
Benzene ring 1	72	79.6	83.4	71.9	79.1	73.1	73.2	89.4	70.4	62.2	49.3	68.7
Benzene ring 2	87	81.1	85.4	71.9	82.1	82.8	79.3	71.3	61.3	87.7	63.9	60.0
Benzene ring 3	90	79.5	72.1	71.9	71.0	79.4	81.3	85.6	80.5	89.1	75.0	81.1

6.466 Å/6.734 Å for the other two ligands, respectively. In the supramolecular complex of 2[TBAH$^+$][AuCl$_4$]$^{2-}$(IX), 5.182 Å/6.656 Å/7.049 Å for one ligand, and 6.422 Å/6.483 Å/6.731 Å for the other ligand. The change of conformation of TBA are to a large extent attributed to the direct hydrogen bonding N–H···Cl interactions between N atoms of TBA and chlorometallates.

In addition, by projecting the molecule on the plane formed by three methylene carbon atoms, the dihedral angles between this plane and benzene rings also exhibit great difference, as listed in Table 2.

Conclusions

In the present contribution, we described two new supramolecular complexes 2[C$_{21}$H$_{22}$N$^+$]·[CoCl$_4$]$^{2-}$ (**1**) and 2[C$_{21}$H$_{22}$N$^+$]·[CuCl$_4$]$^{2-}$ (**2**) by reacting protonated TBA with CoCl$_2$·6H$_2$O/CuCl$_2$·2H$_2$O. Different from previous TBA supramolecular complexes, these two supramolecular complexes were easier to obtain by grinding protonated TBA and CoCl$_2$·6H$_2$O/CuCl$_2$·2H$_2$O in an agate mortar than using conventional solution method. The two supramolecular complexes form fascinating 3D helical architectures, with two types of interwoven helical chains involved inside the structures. A comparison of the geometries of TBA in different supramolecular complexes shows that the significant differences are due to the conformation of the three arms of phenyl rings around the N center.

Acknowledgments This work was supported by the National Science Foundation of China (No. 20903052), Program for Liaoning Excellent Talents in University (No. LJQ 2011003) and Foundation of 211 Project for Innovative Talents Training, Liaoning University.

References

1. Scherl P, Kruckenberg A, Mader S, Wadepohl H, Gade LH (2012) Organometallics 31:7024
2. Wang XJ, Liu YH, Xu CY, Guo QQ, Hou HW, Fan YT (2012) Cryst Growth Des 12:2435
3. Hamacek J, Besnard C, Penhouet T, Morgantini P (2011) Chem Eur J 17:6753
4. Moore CM, Scymczak NK (2012) Dalton Trans 41:7886
5. Atradiotto M, Hesp KD, Lundgren RJ (2010) Angew Chem Int Ed 49:494
6. Canary JW, Mortezaei S, Liang J (2010) Chem Commun 46:5850
7. Martí-Rujas J, Islam N, Hashizume D, Izumi F, Fujita M, Song HJ, Choi HC, Kawano M (2011) Angew Chem Int Ed 50:6105
8. Iwasaki F, Iwasaki H (1972) Acta Crystallogr B28:3370
9. Naikai M, Shirakawa S, Kon-i K, Kondo Y, Maruoka K (2001) Tetrahedron Lett 42:5467
10. Alajarin M, Pastor A, Orenes R-A, Steed JW (2002) J Org Chem 67:7091
11. Chandrasekaran, Day RO, Holmes RR (2000) Inorg Chem 39:5683
12. Groysman S, Segal S, Shamis M, Goldberg I, Kol M, Goldschmidt Z, Hayut-Salant E (2002) J Chem Soc, Dalton Trans 18:3425
13. Alajarin M, Lopez-Lazaro A, Pastor A, Prince PD, Steed JW, Arakawa R (2001) Chem Commun 2:169
14. Jevric M, Zheng T, Meher NK, Fettinger JC, Mascal M (2011) Angew Chem Int Ed 50:717
15. Alajarin M, Pastor A, Orenes RA, Goeta AE, Steed JW (2008) Chem Commun 34:3992
16. Based on the search from the Cambridge Structural Database system, Version 5.33
17. Rosokha SV, Neretin IS, Rosokha TY, Hecht J, Kochi JK (2006) Heteroat Chem 17:449
18. Kozhomuratova ZhS, Naumov NG, Naumov DY, Uskov EM, Fedorov VE (2007) Russ J Coord Chem 33:213
19. Jarvinen GD, Larson EM, Wasserman HJ, Burns CJ, Ryan RR (1988) Acta Crystallogr C44:1701
20. Fazaeli Y, Amani V, Amini MM, Khavasi HR (2010) Acta Crystallogr E66:m212
21. Mohammad Y, Teimouri S, Amani V, Khavasi HR (2007) Acta Crystallogr E63:m2748
22. Guo F, Lu N, Tong J, Luan YB, Guo WS (2010) J Coord Chem 63:809
23. Zeng GF, Qin M, Lin YH, Xi SQ (1994) Acta Crystallogr C50:200
24. Sheldrick GK (1996) SHELXTL reference manual. Siemens Analytical X-ray Systems, Inc., Madison
25. Sheldrick GM (2008) Acta Cryst A64:112
26. James SL, Adams CJ, Bolm C, Braga D, Collier P, Friščić T, Grepioni F, Harris KDM, Hyett G, Jones W, Krebs A, Mack J, Maini L, Orpen AG, Parkin IP, Shearouse WC, Steed JW, Waddell DC (2012) Chem Soc Rev 41:413
27. Karki S, Friščić T, Jones W (2009) CrystEngComm 11:470
28. Based on the search from the Cambridge Structural Database system, Version 5.32