Comparative Analysis of Crystal Structures between 2,2'-Bipyridine and 6,6'-Dimethyl-2,2'-Bipyridine Supported CuSCF₃ Complexes: An Unusual Coordination Transition from Mononuclear to Binuclear Mode

YI YANG^{1,*}, XIA TONG¹, GEN LUO¹, YUMEI SHU¹ and YUBING ZHENG²

¹College of Chemistry and Environmental Engineering, Sichuan University of Science and Engineering, Zigong 643000, P.R. China

²Shandong Jinjing Biological Technology Co., Ltd, Weifang 261313, P.R. China

*Corresponding author: Fax: +86 813 5505606; Tel: +86 813 5505601; E-mail: yangyiyong@163.com

Received: 29 April 2019;

Accepted: 5 June 2019;

Published online: 31 July 2019;

AJC-19509

We report herein the synthesis of CuSCF₃ complex supported by 6,6'-dimethyl-2,2'-bipyridine *via* the strategy of triphenylphosphine-mediated deoxygenation of CF₃SO₂Na in the presence of cuprous chloride. The molecular structure of this new cuprous complex was characterized by elemental analysis, ¹H (¹³C, ¹⁹F) NMR spectra and verified by X-ray crystallography. Unlike the classical [(2,2'-bipyridine)Cu(SCF₃)] complex, 6,6'-dimethyl-2,2'-bipyridine supported cuprous trifluoromethylthiolate complex was dimerized in the form of [(6,6'-dimethyl-2,2'-bipyridine)Cu(SCF₃)₂]₂. The X-ray crystal structure revealed the Cu₂S₂ cyclic pattern and sulfur atoms serving as the bridge. The Cu-Cu distance was equal to 3.083 Å which was remarkably longer than the analogous [(1,10-phenanthroline)Cu(SCF₃)₂]₂ (2.5781(9) Å). This interesting phenomenon demonstrated that the substituents on the ligand scaffolds have profound influence on the coordination modes of these N,N-ligand coordinated CuSCF₃ complexes.

Keywords: Copper, Trifluoromethylthio group, 6,6'-Dimethyl-2,2'-bipyridine, Crystal structure, Binuclear complex.

INTRODUCTION

Transition metal catalyzed (or mediated) direct trifluoromethylthiolation reactions [1-3] have received substantial attentions during the past few years because this privileged functional group (CF₃S-) has broad applications in regulating the chemical and biological properties of diverse classes of pharmaceutical and agrochemical products [4,5]. Generally, these synthetic methods feature the utilization of transition metals as catalysts and the anionic CF₃S- species as the trifluoromethylthiolation reagents. Although important advances have been achieved on this theme [6-10], the limited scope of anionic trifluoromethylthiolation reagents and the restricted combination with transition metal cores still impedes the wide applications of these reaction methodologies in terms of the strong binding and poisoning effects of sulfur atoms towards transition metals. It is therefore of great value to develop transition metal and CF₃S- nucleophile merging reagents.

In this context, the utilization of cuprous trifluoromethylthiolate [CuSCF₃] as direct merging trifluoromethylthiolation

reagents has represented as promising and effective strategy owing to the earth-abundance and sustainability of copper and its interesting functions in transferring CF₃S moieties into aromatic rings [11-15]. Also, it has been proved that the coordination of diverse phosphorus and nitrogen ligands with [CuSCF₃] could lead to novel ligation patterns [LnCu(SCF₃)] and render new reaction profiles in contrast to the unligated [CuSCF₃]. For example, Weng *et al.* [13] disclosed a few types of dinitrogen ligand coordinated [(LN,N)_nCu(SCF₃)] complexes which exhibited air-stability (synthetic practicality) and great potentials in the coupling reactions with aryl halides [13]. Importantly, they found that 2,2'-bipyridine and 1,10-phenanthroline supporting ligands bearing similar structural patterns could give distinct coordination complexes in the ligation steps: one in mononuclear and the other in binuclear coordination mode (Fig. 1A) [13]. Moreover, it was observed that the transition of coordination mode from mononuclear to binuclear coordination pattern remarkably reduced the coupling activities with iodobenzene substrates (Fig. 1B). Therefore, the further exploration of the influences of dinitrogen ligands on the aggregation behaviour

of these $[(\text{LN},\text{N})_n\text{Cu}(\text{SCF}_3)]$ complexes (monomeric or dimeric forms) would be highly intriguing and useful for the optimization of these ligand-regulated cuprous trifluoromethylthiolation reagents. Herein, we describe the novel synthesis of a 6,6'-dimethyl-2,2'-bipyridine supported cuprous trifluoromethylthiolate complex which was surprisingly dimerized in the form of $[\{(6,6'\text{-dimethyl-2,2'-bipyridine})\text{Cu}(\text{SCF}_3)\}_2]$ and make comparative structural analysis with the related monomeric $[(2,2'\text{-bipyridine})\text{Cu}(\text{SCF}_3)]$ and dimeric $[\{(1,10\text{-phenanthroline})\text{Cu}(\text{SCF}_3)\}_2]$ (Fig. 1C).

A. Dinuclear ligand coordinated CuSCF_3 complex

B. Reactivity difference between mononuclear and binuclear CuSCF_3 complex

C. Effects of the *ortho*-groups on the aggregation behavior

Fig. 1. Representative mononuclear and binuclear cuprous trifluoromethylthiolate complexes

EXPERIMENTAL

All the reactions were carried out using standard Schlenk and vacuum-line techniques under N_2 atmosphere. Solvent CH_3CN was distilled from calcium hydride. Cuprous chloride (CuCl), Langlois reagent ($\text{CF}_3\text{SO}_2\text{Na}$), triphenylphosphine (Ph_3P), 6,6'-dimethyl-2,2'-bipyridine were commercially available and used as received. ^1H , ^{13}C and ^{31}P NMR were recorded on a Bruker AM-500 spectrometer. ^{19}F NMR was recorded on another Bruker AM-500 spectrometer (FCF_3 as outside standard and low field is positive). Chemical shifts (δ) are reported in

parts per million and coupling constants (J) are in hertz. Crystallographic data were analyzed with Rigaku FCR diffractometer.

Synthetic procedure: To a solution of $\text{CF}_3\text{SO}_2\text{Na}$ (312 mg, 2.0 mmol) and CuCl (198 mg, 2.0 mmol) in acetonitrile (8 mL, pre-cooled to -20°C) were added Ph_3P (1048 mg, 4.0 mmol). The reaction mixture was stirred under N_2 atmosphere at room temperature for 3–5 h until completion. Then the reaction mixture was filtrated through PTFE filter to remove the insoluble salts and get a clear solution. This solution was frozen ($\sim -20^\circ\text{C}$) for 24 h until the formation of crystalline Ph_3PO . The acetonitrile solution of CuSCF_3 was collected by decanting to remove Ph_3PO and cooled to -20°C again. Then the solution of 6,6'-dimethyl-2,2'-bipyridine (369 mg, 2 mmol) in acetonitrile (6.0 mL) was added in dropwise. The reaction solution was kept at the fridge (-20°C) for crystallization. The resulting crystals were collected by filtration and washed with cold acetonitrile (3 mL, -20°C) and ether (5 mL), and dried under reduced pressure to afford the corresponding $[\{(6,6'\text{-dimethyl-2,2'-bipyridine})\text{Cu}(\text{SCF}_3)\}_2]$ complex (red colour powder, 405 mg, yield: 58 %).

Detection method: Single crystal of $[\{(6,6'\text{-dimethyl-2,2'-bipyridine})\text{Cu}(\text{SCF}_3)\}_2]$ compound suitable for X-ray diffraction analysis can be grown from CH_3CN /pentane solution. The crystal with dimensions of $0.298 \text{ mm} \times 0.169 \text{ mm} \times 0.153 \text{ mm}$ was mounted on a Rigaku RAXIS-RAPID diffractometer equipped with a graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by using an ω scan mode at $293(2) \text{ K}$. Absorption correction was performed by the CRYSTALCLEAR program [16]. The structure was solved by direct methods using the SHELXS-97 program [17] and refined by full-matrix least-squares techniques on F^2 data using SHELXL-97 [18]. The empirical absorption corrections were applied to all intensity data. All the hydrogen atoms were located by using the geometric method, with $d(\text{C-H}) = 0.95\text{--}0.98 \text{ \AA}$ and $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{C})$ or $1.5 \text{ Ueq}(\text{C-methyl})$.

RESULTS AND DISCUSSION

6,6'-Dimethyl-2,2'-bipyridine supported cuprous trifluoromethylthiolate complex could be synthesized *via* the ligation of 6,6'-dimethyl-2,2'-bipyridine with naked CuSCF_3 species which was accessed by our triphenylphosphine-mediated deoxygenative reduction [14,19] of Langlois reagent ($\text{CF}_3\text{SO}_2\text{Na}$) in the presence of CuCl (Scheme-I). The targeted complex was successfully separated from the triphenylphosphine oxide byproduct and isolated in 58 % yield as air-stable red crystals.

To determine the ratio of CF_3SCu and 6,6'-dimethyl-2,2'-bipyridine units of the targeted complex, it was fully characterized by elemental analysis, ^1H , ^{13}C and ^{19}F NMR spectroscopies (For details, see supporting information). The ^{19}F NMR clearly

Scheme-I: Synthetic route towards 6,6'-dimethyl-2,2'-bipyridine supported CuSCF_3 complex

indicated the presence of CF_3S moiety and the binding to Cu core. Elemental analysis results verified the CF_3SCu and 6,6'-dimethyl-2,2'-bipyridine fragments in the ratio of 1:1. Interestingly, the methyl groups in ^1H NMR displayed as broad peaks which might be explained by its proximity to paramagnetic copper core.

For elucidating the coordination mode of 6,6'-dimethyl-2,2'-bipyridine supported cuprous trifluoromethylthiolate complex, the single crystals was grown from a CH_3CN /pentane solution and the dimeric molecular form was determined by the X-ray diffraction analysis. ORTEP and crystal packing diagram of compound **3** are shown in Figs. 2 and 3, respectively and crystallographic and refinement parameters of the title compound **3** are listed in Table-1. The selected bond lengths and angles are given in Tables 2-3. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all nonhydrogen atoms in full-matrix least-square refinements based on F^2 . The hydrogen atoms were set in calculated positions with a common fixed isotropic thermal parameter.

Fig. 2. ORTEP view of compound **3** (hydrogen atoms were omitted for clarity)

Fig. 3. Crystal packing diagram (Wireframe) of compound **3** (hydrogen atoms were omitted for clarity)

With the X-ray crystal structure of $[(6,6'\text{-dimethyl-2,2'-bipyridine})\text{Cu}(\text{SCF}_3)]_2$ complex established, the comparative structural analysis *versus* mononuclear $[(2,2'\text{-bipyridine})\text{Cu}(\text{SCF}_3)]$ (**1**) and binuclear $[(1,10\text{-phenanthroline})\text{Cu}(\text{SCF}_3)]_2$ (**1**) was conducted. Firstly, although the basic supporting scaffolds of the ligands **1** and **3** are 2,2'-bipyridine, the aggregation behaviours of these complexes are quite dissimilar. Like the binuclear $[(1,10\text{-phenanthroline})\text{Cu}(\text{SCF}_3)]_2$ (**2**), complex **3** also packed in the dimeric form within crystal lattice. It should also be noted that Cu-S bonds in complex **3** display

TABLE-1
CRYSTAL DATA AND STRUCTURAL
REFINEMENT FOR COMPOUND **3**

Items	Values
Empirical formula	$\text{C}_{26}\text{H}_{24}\text{N}_4\text{S}_2\text{Cu}_2\text{F}_6$
Formula weight	697.71
Crystal system	Monoclinic
Unit cell dimensions	
a (Å)	8.8954(7)
b (Å)	17.9393(15)
c (Å)	8.5445(7)
Unit cell angles (°)	
α	90
β	104.992(2)
γ	90
Volume (Å ³)	1317.1
Z	4
Space group	$P 2_1/c$

TABLE-2
SELECTED BOND LENGTHS (Å) FOR COMPOUND **3**^a

Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
Cu(1)-N(1)	2.073(2)	C(1)-F(2)	1.349(3)
Cu(1)-N(2)	2.076(2)	C(1)-F(3)	1.341(3)
Cu(1)-S(1)	2.2958(7)	C(1)-S(1)	1.765(3)
Cu(1)-S(1')	2.4026(7)	C(2)-C(7)	1.488(4)
C(1)-F(1)	1.347(4)	C(12)-C(13)	1.489(4)

^aThe prime atoms belong to the half unit of $[(6,6'\text{-dimethyl-2,2'-bipyridine})\text{Cu}(\text{SCF}_3)]_2$ on the right side.

TABLE-3
SELECTED BOND ANGLES (°) FOR COMPOUND **3**^a

Bond	Bond angles (°)	Bond	Bond angles (°)
N(1)-Cu(1)-N(2)	80.46(9)	F(2)-C(1)-F(3)	105.1(2)
N(1)-Cu(1)-S(1)	117.74(6)	F(1)-C(1)-S(1)	114.9(2)
S(1)-Cu(1)-S(1')	98.00(2)	F(2)-C(1)-S(1)	113.2(2)
Cu(1)-S(1)-Cu(1')	82.00(2)	F(3)-C(1)-S(1)	113.3(2)
F(1)-C(1)-F(2)	104.5(2)	Cu(1)-S(1)-C(1)	110.46(9)
F(1)-C(1)-F(3)	104.9(2)	Cu(1)-S(1)-C(1')	113.89(9)

^aThe prime atoms belong to the half unit of $[(6,6'\text{-dimethyl-2,2'-bipyridine})\text{Cu}(\text{SCF}_3)]_2$ on the right side.

unsymmetrical distances (2.296 Å and 2.403 Å) which are quite distinct from that of the binuclear complex **2** (symmetrical bond lengths: 2.330 Å). Namely, the planar Cu_2S_2 cycle in complex **3** was a simple parallelogram unlike the lozenge pattern of complex **2**. On the other hand, Cu(1)-N(1) and Cu(1)-N(2) lengths in complex **3** are also unequal (2.073 Å and 2.076 Å, Fig. 4) which is a distinguishing feature of these bipyridine-supported CuSCF_3 complexes. However, both Cu(1)-N(1) and Cu(1)-N(2) lengths in complex **2** are equal to 2.062 Å. Finally, the Cu-Cu separation within the Cu_2S_2 ring of complex **3** is 3.083 Å which is significantly longer than the distance of 2.578 Å in complex **2**. Taken together, the above observed structural characteristics of complex **3** *versus* complexes **1** and **2** suggest that *ortho*-methyl groups neighbouring to Cu-N coordination bond are highly responsible for the transition of coordination modes from the common mononuclear to binuclear. The electronic interactions between the methyl groups and CuSCF_3 motifs and the resultant distortions (N(2)-Cu(1)-N(1)-

Fig. 4. Short contacts within the crystal lattice of compound **3**

C(6), distortion angle $-10.2(2)^\circ$; Cu(1)-N(2)-C(12)-C(13), distortion angle $-6.3(4)^\circ$ within the crystal lattice could be corresponded to the *ortho* effects [20–22] in many aspects of physical organic chemistry.

Further studies on the secondary interactions within the crystal lattices were carried out. Along with previous observations of F···H interactions in several organofluorine compounds [23,24], complex **3** also exhibited the electrostatic contacts between the fluorine atoms (F(2)/F(3)) and the hydrogen atoms on the ligand scaffold. For example, the F(2) atom contacted with the H(00E) atom in a distance of 2.477 Å under the combinatorial interaction of H(00E)···S(1). On the other hand, F(3) atom also interacted with the aliphatic H(00F) of methyl and aromatic H(00D) simultaneously. In addition, the short contacts of C(8)···C(5) and C(6)···C(4) were observed which could be elucidated by the π - π stacking between the aromatic rings. Evidently, these secondary interactions including F···H electrostatic contacts and π - π stackings played important roles in the spatial arrangements in the crystal lattices.

Conclusion

In conclusion, we have described the efficient synthesis of binuclear [(6,6'-dimethyl-2,2'-bipyridine)Cu(SCF₃)₂]₂ complex **3** via the deoxygenative reduction of Langlois reagent and its full structural characterization. The comparative study of X-ray crystal structures among complexes **1–3** demonstrated that the coordination modes of these dinitrogen ligated cuprous trifluoromethylthiolate complexes were highly influenced by the fine structures of supporting ligands. The investigations on the short contacts within the crystal lattice of complex **3** revealed the presence of H···F electrostatic forces and π - π stacking interactions. It is believed that these interesting structural features could be valuable for the design, synthesis and application of more transition metal trifluoromethylthiolate complexes as well as the related trifluoromethylthiolation reaction development.

Supplementary data L: CCDC-1428919 contains the supplementary crystallographic data of [(6,6'-dimethyl-2,2'-bipyridine)Cu(SCF₃)₂]₂ for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; or E-mail: deposit@ccdc.cam.ac.uk).

ACKNOWLEDGEMENTS

The authors thank National Natural Science Foundation of China (21502131), Science & Technology Department of Sichuan Province (2018JZ0061, 2018HH0128), Education Department of Sichuan Province (18CZ0024), Key Laboratory of Vanadium and Titanium of Sichuan Province (2018FTSZ03), Sichuan University of Science and Engineering (2017RCL03) and Sichuan Youth Plan for financial support.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- X.-H. Xu, K. Matsuzaki and N. Shibata, *Chem. Rev.*, **115**, 731 (2015); <https://doi.org/10.1021/cr500193b>.
- L. Chu and F.-L. Qing, *Acc. Chem. Res.*, **47**, 1513 (2014); <https://doi.org/10.1021/ar4003202>.
- H. Zheng, Y. Huang and Z. Weng, *Tetrahedron Lett.*, **57**, 1397 (2016); <https://doi.org/10.1016/j.tetlet.2016.02.073>.
- V.N. Boiko, *Beilstein J. Org. Chem.*, **6**, 880 (2010); <https://doi.org/10.3762/bjoc.6.88>.
- F. Toulgoat, S. Alazet and T. Billard, *Eur. J. Org. Chem.*, 2415 (2014); <https://doi.org/10.1002/ejoc.201301857>.
- G. Teverovskiy, D.S. Surry and S.L. Buchwald, *Angew. Chem. Int. Ed.*, **50**, 7312 (2011); <https://doi.org/10.1002/anie.201102543>.
- G. Yin, I. Kalvet and F. Schoenebeck, *Angew. Chem. Int. Ed.*, **54**, 6809 (2015); <https://doi.org/10.1002/anie.201501617>.
- K.-Y. Ye, X. Zhang, L.-X. Dai and S.-L. You, *J. Org. Chem.*, **79**, 12106 (2014); <https://doi.org/10.1021/jo5019393>.
- G. Yin, I. Kalvet, U. Englert and F. Schoenebeck, *J. Am. Chem. Soc.*, **137**, 4164 (2015); <https://doi.org/10.1021/jacs.5b00538>.
- C.-P. Zhang and D.A. Vovic, *J. Am. Chem. Soc.*, **134**, 183 (2012); <https://doi.org/10.1021/ja210364r>.
- J.H. Clark, C.W. Jones, A.P. Kybett, M.A. McClinton, J.M. Miller, D. Bishop and R.J. Blade, *J. Fluor. Chem.*, **48**, 249 (1990); [https://doi.org/10.1016/S0022-1139\(00\)80437-6](https://doi.org/10.1016/S0022-1139(00)80437-6).
- J.H. Clark and H. Smith, *J. Fluor. Chem.*, **61**, 223 (1993); [https://doi.org/10.1016/S0022-1139\(00\)80106-2](https://doi.org/10.1016/S0022-1139(00)80106-2).
- Z. Weng, W. He, C. Chen, R. Lee, D. Tan, Z. Lai, D. Kong, Y. Yuan and K.-W. Huang, *Angew. Chem. Int. Ed.*, **52**, 1548 (2013); <https://doi.org/10.1002/anie.201208432>.
- Y. Yang, L. Xu, S. Yu, X. Liu, Y. Zhang and D.A. Vovic, *Chem. Eur. J.*, **22**, 858 (2016); <https://doi.org/10.1002/chem.201504790>.
- M. Rueping, N. Tolstoluzhsky and P. Nikolaenko, *Chem. Eur. J.*, **19**, 14043 (2013); <https://doi.org/10.1002/chem.201302692>.
- Crystal Clear and Crystal Structure, Rigaku and Rigaku Americas. 9009 New Trails Dr. The Woodlands TX 77381 USA.
- G.M. Sheldrick, SHELXS97, A Program for Crystal Structure Solution, University of Göttingen: Germany (1997).
- G.M. Sheldrick, SHELXS97, A Program for Crystal Structure Refinement, University of Göttingen: Germany (1997).
- L. Jiang, Y. Qian, W. Yi, G. Lu, C. Cai and W. Zhang, *Angew. Chem. Int. Ed.*, **54**, 14965 (2015); <https://doi.org/10.1002/anie.201508495>.
- M. Charton, *Progr. Phys. Org. Chem.*, **8**, 235 (1971).
- T. Fujita and T. Nishioka, *Progr. Phys. Org. Chem.*, **13**, 49 (1976).
- M. Charton, *J. Am. Chem. Soc.*, **91**, 615 (1969); <https://doi.org/10.1021/ja01031a016>.
- Y. Yang, Y.-L. Li, C.-R. Cheng, Z.-W. Deng, Y.-P. Liu and W. Yuan, *Asian J. Chem.*, **26**, 2748 (2014); <https://doi.org/10.14233/ajchem.2014.16492>.
- Y. Yang, Y.-L. Li, Y. Jiang, J.-Z. Li, Z.-W. Deng and C.-R. Cheng, *Asian J. Chem.*, **26**, 3077 (2014); <https://doi.org/10.14233/ajchem.2014.16746>.