NOTE

Synthesis and Crystal Structure of $[\text{Cu}_2(\text{TTA})_4(4,4'\text{-bpy})]$

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A new complex, $[\text{Cu}_2(\text{TTA})_4(4,4'\text{-bpy})]$ (TTA = 2-thenoyl-trifluoroacetone, bpy = bipyridine) with the molecular formula $\text{C}_{42}\text{H}_{28}\text{N}_2\text{O}_8\text{S}_4\text{F}_{12}\text{Cu}_2$ has been synthesized and structurally characterized by elemental analysis, IR spectrum and X-ray diffraction analysis. The crystal belongs to triclinic system, P-1 group with unit cell parameters: $a = 8.5755(7) \text{ \AA}$, $b = 10.2215(8) \text{ \AA}$, $c = 13.9964(12) \text{ \AA}$, $\alpha = 72.548(3)^\circ$, $\beta = 85.407(3)^\circ$, $\gamma = 86.130(3)^\circ$. $V = 1165.4(17) \text{ \AA}^3$, $Z = 1$, $M_r = 1172.04$, $D_c = 1.6700(2) \text{ g/cm}^3$, $\mu = 1.193 \text{ mm}^{-1}$, $F(000) = 588.0$, $R = 0.0601$, $wR = 0.1889$ for 4044 reflections with $I > 2\sigma(I)$.

Key Words: Copper(II), 4,4'-Bipyridine, 2-Thenoyltrifluoroacetone, Crystal structure.

In past decades, researches of hybrid material combining metallic centers together with organic moieties have grown exponentially¹. β -diketone ligands are an excellent metal chelator and it has a wide range of applications in functional materials, such as liquid crystal materials, non-linear optical materials, luminescent materials, *etc.*²⁻⁴. 4,4'-Bipyridine, an excellent rigid bridging ligand, both ends of the nitrogen atoms can coordinate with different metal atoms simultaneously. Furthermore, it is liable to form some weak intermolecular interactions such as hydrogen bondings or π - π stacking interactions with other molecules. 4,4'-Bipyridine can form a variety of one-dimensional⁵, two-dimensional⁶ and three-dimensional⁷ structure of the complexes with metal ions. Most of these complexes have a larger cavity or pipe so that they possess the ability of inclusions for some bulky organic molecules in the aspects of molecular recognition^{8,9}, these features can be used for material separation and purification, catalysis of chemical reactions and ion exchange, *etc.*¹⁰. Moreover, owing to the special magnetic properties, some complexes can be used as special magnetic materials¹¹. In this paper, we reported the synthesis of a new complex $[\text{Cu}_2(\text{TTA})_4(4,4'\text{-bpy})]$ and presented its crystal structure.

Synthesis of $[\text{Cu}_2(\text{TTA})_4(4,4'\text{-bpy})]$: A mixture of 2-thenoyltrifluoroacetone (444 mg, 2 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (242 mg, 1 mmol) were dissolved in anhydrous alcohol (20 mL), the mixture was stirred for 0.5 h at room temperature, then 4,4'-bipyridine (78 mg, 0.5 mmol) was added and the mixture was refluxed for 2 h. After cooling to room temperature, green single crystals suitable for X-ray diffraction analysis

were obtained by slow evaporation at room temperature. IR (KBr, ν_{max} , cm^{-1}): 1596 (s), 1541 (w), 1408 (w); 1317 (w); 1144 (w). Anal. calcd. (%) for $[\text{Cu}_2(\text{TTA})_4(4,4'\text{-bpy})]$: m.f. $\text{C}_{42}\text{H}_{28}\text{N}_2\text{O}_8\text{S}_4\text{F}_{12}\text{Cu}_2$, C, 43.06; H, 2.43; N, 2.40. Found (%): C, 43.46; H, 2.45; N, 2.38.

Crystal structure determination: The X-ray data were collected on a Bruker Apex-II CCD diffractometer using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 (2) K with crystal size $0.17 \text{ mm} \times 0.13 \text{ mm} \times 0.12 \text{ mm}$. A total of 4044 ($R_{\text{int}} = 0.0248$) independent reflections were collected by ϕ and ω scans technique in the range of $1.53 \leq \theta \leq 25.00^\circ$ from which 3444 [$I > 2\sigma(I)$] reflection were corrected for Lorentz and polarization factors. The structure was solved by direct method using SHELXS-97¹² and refined using a full-matrix least-squares procedure on F^2 in SHELXS-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added theoretically and refined with riding model (Tables 1-3).

Fig. 1 shows the molecular structure of the complex $\text{Cu}_2(\text{TTA})_4(4,4'\text{-bpy})$. The selected bond lengths and bond angles are given in Table-2, C-H... π and C-F... π interactions are listed in Table-3. The structure revealed that Cu centers adopted square pyramid coordination geometries, Cu1 ions were five coordinated by O1, O2, O3, O4 atoms from two 2-thenoyltrifluoroacetone molecules and N1 atoms from one end of a 4,4'-bipyridine molecules, the other end of the 4,4'-bipyridine bridged the Cu1' central ions by N1' atoms. The distance of Cu-N bond was $2.285(4) \text{ \AA}$, distances of Cu-O bonds varied from $1.932(3)$ to $1.948(3) \text{ \AA}$, bonds angles of

TABLE-I
 CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY

Formula	C ₄₂ H ₂₈ N ₂ O ₈ S ₄ F ₁₂ Cu ₂	Volume (Å ³)	1165.40(17)
Formula weight	1172.04	Z	1
Crystal system	Triclinic	D (calc.), (g cm ⁻³)	1.6700(2)
Space group	P -1	M (mm ⁻¹)	1.193
Temperature (K)	293(2)	F(000)	588.0
Limiting indices	-9 ≤ h ≤ 10 -12 ≤ k ≤ 12 -16 ≤ l ≤ 16	θ range (°)	0.985 ≤ θ ≤ 25.00
Unit cell dimensions (Å)	a = 8.5755(7)	Reflection collected	4044
	b = 10.2215(8)	Independent reflection	3444
	c = 13.9964(12)	R _{int}	0.0248
		Final R indices	R ₁ = 0.0601
		[I > 2σ(I)]	wR ₂ = 0.1889

O1-Cu1-O2, O2-Cu1-O3, O3-Cu1-O4, O4-Cu1-O1, N1-Cu1-O1, N1-Cu1-O2, N1-Cu1-O3, N1-Cu1-O4 was 92.94(13), 86.60(14), 92.72(13), 85.75(13), 90.72(14), 98.81(15), 99.76(15), 91.98(14)°, respectively. It is worth noting that the chelating rings of Cu1, O1, O2, C2, C3, C4 and Cu1, O3, O4, C10, C11, C12 is not coplanar, the dihedral angle is 16.23°. Furthermore, intermolecular extensive C-H...π and C-F...π interactions have been found in the structure, they act as vital roles in the stabilizations of complex crystal.

Fig. 1. Molecular structure of Cu₂(TTA)₄·(4,4'-bpy)
 TABLE-2
 SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Cu1-N1	2.285(4)	S2-C8	1.678(7)	O1-Cu1-O2	92.94(13)
Cu1-O1	1.948(3)	C1-F6	1.306(9)	O2-Cu1-O3	86.60(14)
Cu1-O2	1.932(3)	O1-C4	1.272(5)	N1-Cu1-O3	99.76(15)
Cu1-O3	1.947(4)	N1-C17	1.296(8)	N1-Cu1-O4	91.98(14)
Cu1-O4	1.939(3)	N1-C21	1.326(6)	C16-S1-C13	92.3(3)
S2-C5	1.711(5)	C19-C19'	1.471(6)	F4-C1-F5	106.9(6)

 TABLE-3
 C-H...π AND C-F...π INTERACTIONS
 DISTANCES (Å) AND ANGLES (°)

Type (Y-X...Cg)	d (X...Cg)	∠(YXCg)	d (Y...Cg)	Symmetry code
C15-H15...Cg5	3.00	142.00	3.777(8)	x, 1+y, z
C9-F3...Cg4	3.968(7)	119.2(4)	4.735(7)	1-x, 1-y, -z
C9-F3...Cg5	3.622(6)	170.5(5)	4.902(7)	1-x, 1-y, -z
C1-F5...Cg2	3.936(6)	134.2(5)	4.936(7)	-1+x, y, z

Conclusion

A new dinuclear complex [Cu₂(TTA)₄·(4,4'-bpy)] has been synthesized with 2-thenoyltrifluoroacetone, 4,4'-bipyridine and Cu(NO₃)₂·3H₂O. The crystal shows two square pyramid coordination centers of Cu ions, 4,4'-bpy functions as a bridged ligand in the formation of the complex, intermolecular C-H...π and C-F...π interactions stabilize the crystal.

Supplementary material: Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 860017.

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REFERENCES

- See themed issue, Metal-Organic Frameworks, **38**, 1201 (2009).
- H. Xu, K. Yin and W. Huang, *J. Phys. Chem. C*, **114**, 1674 (2010).
- P.P. Sun, J.P. Duan and H.T. Shih, *Appl. Phys. Lett.*, **81**, 792 (2000).
- R.N. Yang, D.M. Wang and C.Y. Li, *Chin. J. Inorg. Chem.*, **17**, 209 (2001).
- R.W. Gable, B. Hoskins and G. Winter, *Inorg. Chim. Acta*, **96**, 151 (1985).
- X.M. Chen, M.L. Tong and Y.J. Luo, *Aust. J. Chem.*, **49**, 835 (1996).
- G.B. Gardner, D. Venkataraman and J.S. Moore, *Nature*, **374**, 792 (1995).
- M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, **112**, 5645 (1990).
- M. Fujita, Y.J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, **116**, 1151 (1994).
- O.M. Yaghi and H.L. Li, *J. Am. Chem. Soc.*, **117**, 10401 (1995).
- M.A. Lawandy, X. Huang, R.J. Wang, J. Li, J.Y. Lu, T. Yuen and C.L. Lin, *Inorg. Chem.*, **38**, 5410 (1999).
- G.M. Sheldrick, SHELXL-97 Program for the Solution and Refinement of Crystal structures, University of Göttingen, Germany (1997).