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NOTE

Synthesis and Crystal Structure of $[Cu_2(TTA)_4 \cdot (4,4'\text{-bpy})]$

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A new complex, $[Cu_2(TTA)_4 \cdot (4,4'\text{-bpy})]$ (TTA = 2-thenoyl-trifluoracetone, bpy = bipyridine) with the molecular formula $C_{42}H_{28}N_2O_8S_4F_{12}Cu_2$ 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) Å, b = 10.2215(8) Å, c = 13.9964(12) Å, α = 72.548 (3)º, β = 85.407 (3)º, γ = 86.130 (3)º. V=1165.4 (17) Å^3, Z = 1, Mr = 1172.04, Dc = 1.6700 (2) g/cm^3, μ = 1.193 mm^{-1}, F (000) = 588.0, R = 0.0601, wR = 0.1889 for 4044 reflections with I > 2σ (I).

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

In past decades, researches of hybrid material combining metallic centers together with organic moieties have grown exponentially[1]. 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 formed a variety of one-dimensional[5], two-dimensional[6] and three-dimensional[7] 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, owning to the special magnetic properties, some complexes can be used as special magnetic materials[11]. In this paper, we reported the synthesis of a new complex $[Cu_2(TTA)_4 \cdot (4,4'\text{-bpy})]$ and presented its crystal structure.

Synthesis of $[Cu_2(TTA)_4 \cdot (4,4'\text{-bpy})]$: A mixture of 2-thenoyltrifluoracetone (444 mg, 2 mmol) and $Cu(NO_3)_2.3H_2O$ (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 $[Cu_2(TTA)_4 \cdot (4, 4'\text{-bpy})]$: m.f. $C_{42}H_{28}N_2O_8S_4F_{12}Cu_2$, 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 MoK_α radiation (λ = 0.71073Å) at 293 (2) K with crystal size 0.17 mm × 0.13 mm × 0.12 mm. A total of 4044 (R_{int} = 0.0248) independent reflections were collected by φ and ω scans technique in the range of 1.53 ≤ θ ≤ 25.00º from which 3444 [I > 2σ (I)] reflection were corrected for Lorentz and polarization factors. The structure was solved by direct method using SHELXS-97[12] 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 $Cu_2(TTA)_4 \cdot (4,4'\text{-bpy})$. 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-thenoyltrifluoracetone 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) Å, distances of Cu-O bonds varied from 1.932(3) to 1.948(3) Å, bonds angles of

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY

Formula	$C_{42}H_{28}N_2O_8S_4F_{12}Cu_2$	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	$-9 \le h \le 10$	θ range (º)	$0.985 \le \theta \le 25.00$
	$-12 \le k \le 12$	Reflection collected	4044
	$-16 \le l \le 16$	Independent reflection	3444
Unit cell dimensions (Å)	a = 8.5755(7)	R_{int}	0.0248
	b = 10.2215(8)	Final R indices	$R_1 = 0.0601$
	c = 13.9964(12)	[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)º, 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 angel is 16.23º. 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.

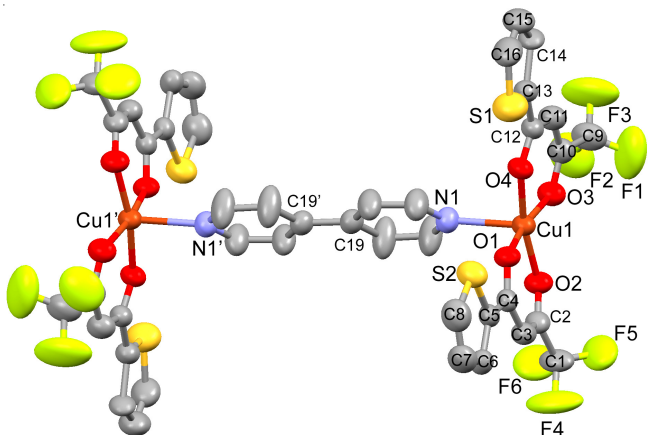

Fig. 1. Molecular structure of $Cu_2(TTA)_4$·(4,4'-bpy)

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (º)

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 (º)

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 $[Cu_2(TTA)_4$·(4,4'-bpy)] has been synthesized with 2-thenoyltrifluoracetone, 4,4'-bipyridine and $Cu(NO_3)_2.3H_2O$. 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.

Supplymentry 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

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