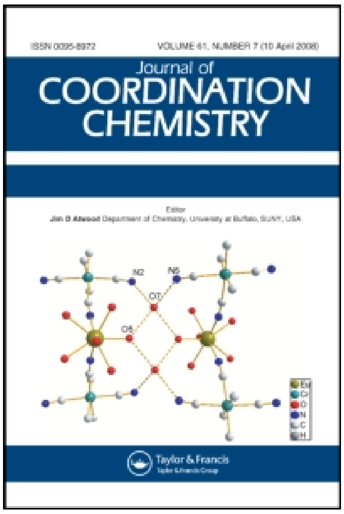

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Marandi, Farzin , Soudi, Ali A. , Morsali, Ali and Zhu, Long-Guan(2007) 'Cd^{II} 4,4,4-trifluoro-1-phenyl-1,3-butandione complexes of 1,10-phenanthroline and 4,4'-bipyridine', Journal of Coordination Chemistry, 60: 19, 2107 — 2114

To link to this Article: DOI: 10.1080/00958970701244747

URL: http://dx.doi.org/10.1080/00958970701244747

Journal of Coordination Chemistry
Vol. 60, No. 19, 1 October 2007, 2107–2114

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Cd^{II} 4,4,4-trifluoro-1-phenyl-1,3-butandione complexes of 1,10-phenanthroline and 4,4′-bipyridine

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(*Received 26 November 2006; revised 19 December 2006; in final form 27 December 2006*)

Cadmium(II) 4,4,4-trifluoro-1-phenyl-1,3-butandione (HTFPB) complexes of 1,10-phenanthroline (phen) and 4,4′-bipyridine (4,4′-bipy), $Cd(L)(TFPB)_2$, have been synthesized and characterized by elemental analysis, IR-, ^1H NMR spectroscopy and X-ray crystallography. The self-assembly of $Cd(L)(TFPB)_2$ complexes, (L = phen or 4,4′-bipy) is caused by $C–H \cdots F–C$, and π–π stacking interactions.

Keywords: Cadmium; 4,4,4-Trifluoro-1-phenyl-1,3-butandione; π–π-Stacking; 1,10-Phenanthroline; 4,4′-Bipyridine; $C–H \cdots F–C$ interaction

1. Introduction

Supramolecular chemistry is one of the topical fields of contemporary chemistry and supramolecules are often self-assembled systems by means of a variety of intermolecular non-covalent interactions [1]. Research on coordination polymers and applications such as luminescent, magnetic, polycatenated and polythreaded coordination polymers has progressed very rapidly over the last two decades [2]. Design of new coordination polymers and supramolecular materials by precise topological control generated through intermolecular interactions are the goal. β-Dicarbonyl compounds are an important class of ligands [3, 4], versatile and exhibit a great variety of coordination modes [5]. Equilibrium mixtures of tautomeric keto and enol forms β-diketones could be favored by replacement of terminal groups by electron-withdrawing or electron-releasing substituents [6].

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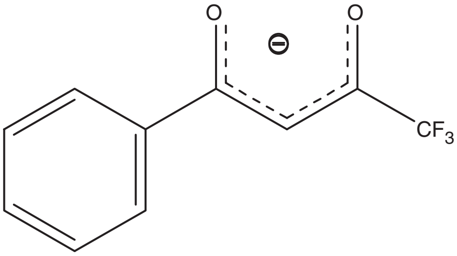
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970701244747

From structural studies of different compounds involving fluorine atoms [7, 8], it has been argued that C–H $\cdots$ F, F $\cdots$ F and C–F $\cdots \pi$ interactions [7–9] play an important role in solid state lattices of such compounds, so that it was anticipated that this might be true for Cd^{II} complexes of 4,4,4-trifluoro-1-phenyl-1,3-butandione (HTFPB).

The present determination of the structures Cd^{II} 4,4,4-trifluoro-1-phenyl-1,3-butandione (HTFPB) complexes of 1,10-phenanthroline (phen) and 4,4′-bipyridine (4,4′-bipy) provide supramolecular compounds involving CH $\cdots$ F–C, π–π stacking.



TFPB$^-$

2. Experimental

2.1. *Physical measurements*

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O- Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz.

2.2. *Preparation of [Cd(4,4′-bipy)(TFPB)$_2$]$_n$ (1)*

4,4′-Bipyridine (0.156 g, 1 mmol) was placed in one arm of a branched tube and cadmium(II) acetate (0.230 g, 1 mmol), and “HTFPB” (0.432 g, 2 mmol) in the other. Methanol was carefully added to fill both arms, the tube sealed and the ligand-containing arm immersed in a bath at 60° while the other was at ambient temperature. After 3 days, crystals had deposited in the cooler arm which were filtered off, washed with acetone and ether, and air dried, yield: 0.490 g, 70%, m.p. >300°. (Found C, 51.80; H, 2.65; N, 3.66; calculated for $C_{30}H_{20}CdF_6N_2O_4$: C, 51.51; H, 2.86; N, 4.91%.

IR (cm^{-1}) selected bands: 632(m), 709(m), 809(m), 1133(s), 1187(s), 1288(vs), 1473(s), 1535(s), 1612(vs), and 3062(w).

^{1}H NMR (DMSO, δ 7.55(m, 6H), 7.95(m, 4H), 6.25(s, 2H), 7.85(d, 4H), 8.75(d, 4H).

2.3. *Preparation of Cd(phen)(TFPB)$_2$ (2)*

1,10-Phenanthroline (0.2 g, 1 mmol) was placed in one arm of a branched tube and cadmium(II) acetate (0.230 g, 1 mmol), and “HTFPB” (0.432 g, 2 mmol) in the other. Methanol was carefully added to fill both arms, the tube sealed and the ligand-containing arm immersed in a bath at 60° while the other was at ambient temperature. After 3 days, crystals had deposited in the cooler arm, which were filtered off, washed with acetone and ether, and air dried, yield: 0.542 g, 75%, m.p. 182°. (Found C, 53.80; H, 2.65; N, 3.56, calculated for $C_{32}H_{20}CdF_6N_2O_4$: C, 53.11; H, 2.76; N, 3.87%.

IR (cm^{-1}) selected bands: 721(m), 758(m), 1025(m), 1160(s), 1288(vs), 1465(s), 1573(s), 1621(vs), and 3065(w).

^1H NMR (DMSO, δ): 7.45(m, 6H), 7.80(m, 2H), 8.15(m, 2H), 6.15(s, 2H), 7.75(t, 2H), 8.20(t, 2H), 8.85(d, 2H), 9.15(d, 2H).

2.4. *Crystallography*

Crystallographic measurements were made at 295(2) K for **1** and **2** using a Siemens R3m V^{-1} diffractometer. The intensity data were collected within the range 1.84–27.00° for **1** and 1.30 to 25.50° for **2** using graphite monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2. Structure solution and refinement was accomplished using SIR97, SHELXL97 and WinGX [10, 11].

Crystal data and structure refinements are given in table 1. Selected bond lengths and angles are given in table 2. Anisotropic thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagrams and perspective views of the packing are shown in figures 1–4.

3. Results and discussion

The crystal structure of **1** consists of one-dimensional polymeric units of [Cd(4,4′-bipy)$(TFPB)_2$]. The nitrogen atoms of 4,4′-bipy are linked to two different cadmium atoms and also the $TFPB^-$ anions are coordinated to cadmium and do not bridge. The coordination number in this complex is six (two from 4,4′-bipy ligands and four oxygens of two $TFPB^-$ anions) and the coordination around Cd is distorted octahedral. The cadmium atoms are only bridged by 4,4′-bipy producing one-dimensional polymeric units. Since the inversion center is not located at the middle of the C13–C16 bond, the aromatic rings of 4,4′-bipy are not coplanar. The two 4,4′-bipy and two $TFPB^-$ anions are trans-substituted, the N(1)–Hg(1)–N(2) angle is 180.0(4)°, and the structural supramolecular isomer is the 1D open framework structure [12].

Single X-ray crystal analysis reveals that the complex **2** are monomeric units (figure 2) and the Cd atom is coordinated by six donors from three different ligands (two nitrogen atoms of the one 1,10-phenanthroline and four oxygen atoms of two $TFPB^-$ anions), the resulting geometry around the Cd atom being distorted octahedral.

A search was made for C–H ··· F–C approaches in **1** and **2**. There are C–H ··· F–C weak hydrogen bonding interactions between the hydrogen atoms of aromatic ligands (4,4′-bipy in **1** and phen in **2** and fluorine atoms belonging to $TFPB^-$ anions of adjacent complexes, as shown in figures 3–4. In 1 (figure 3), there are two different C–H ··· F–C interactions between fluorine atoms of $TFPB^-$ and hydrogen atoms of phenyl (ph)

Table 1. Crystal data and structure refinement for [Cd(4,4′-bipy)(TFPB)$_2$]$_n$ (**1**) and [Cd(phen)(TFPB)$_2$] (**2**).

Identification code	[Cd(4,4′-bipy)(TFPB)$_2$]$_n$	[Cd(phen)(TFPB)$_2$]
Empirical formula	$C_{30}H_{20}CdF_6N_2O_4$	$C_{32}H_{20}CdF_6N_2O_4$
Formula weight	698.88	722.90
Temperature (K)	295(2)	295(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	Fdd2	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	44.173(10)	9.0594(5)
b	11.396(2)	10.9482(6)
c	11.726(2)	15.8562(9)
α		94.4820(10)
β		94.8920(10)
γ		104.9380(10)
Volume (Å^3)	5903(2)	1505.79(14)
Z	8 2	2
Density (calculated) (Mg m^{-3})	1.573	1.594
Absorption coefficient (mm^{-1})	0.815	0.802
F(000)	2784	720
Crystal size (mm^3)	0.20 × 0.10 × 0.03	0.17 × 0.17 × 0.25
θ range for data collection (°)	1.84–27.00	1.30–25.50
Index ranges	$-56 \le h \le 56$; $-14 \le k \le 14$; $-14 \le l \le 14$	$-10 \le h \le 10$; $-13 \le k \le 13$; $-19 \le l \le 19$
Reflections collected	12095	11357
Independent reflections	3226 [R(int) = 0.0469]	5532 [R(int) = 0.0161]
Completeness to theta (%)	100.0	98.8
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	3226/1/197	5532/0/406
Goodness-of-fit on F^2	1.076	1.116
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0430$, $wR_2 = 0.1015$	$R_1 = 0.0411$, $wR_2 = 0.1099$
R indices (all data)	$R_1 = 0.0493$, $wR_2 = 0.1054$	$R_1 = 0.0433$, $wR_2 = 0.1119$
Largest diff. peak, hole (e Å)	0.595, −0.300	1.137, −0.347

Table 2. Bond lengths (Å) and angles (°) for [Cd(4,4′-bipy)(TFPB)$_2$]$_n$ (**1**) and [Cd(phen)(TFPB)$_2$] (**2**).

[Cd(4,4′-bipy)(TFPB)$_2$]$_n$ (**1**)		[Cd(phen)(TFPB)$_2$] (**2**)	
Cd–O1	2.26(3)	Cd–O3	2.24(3)
Cd–O2	2.27(3)	Cd–O1	2.25(3)
Cd–N2	2.31(1)	Cd–O2	2.25(3)
Cd–N1	2.35(1)	Cd–O4	2.31(2)
O1–Cd–O1	168.2(2)	Cd–N2	2.32(3)
O1–Cd–O2	97.2(1)	Cd–N1	2.33(3)
O1–Cd–O2	82.7(1)	O3–Cd–O1	83.9(1)
O1–Cd–N2	95.9(1)	O3–Cd–O2	100.4(1)
O2–Cd–N2	90.7(1)	O1–Cd–O2	80.7(9)
O1–Cd–N1	84.1(1)	O3–Cd–O4	78.3(1)
O2–Cd–N1	89.3(1)	O1–Cd–O4	159.8(1)
N2–Cd–N1	180.0(4)	O2–Cd–O4	93.2(1)
		O3–Cd–N2	99.1(1)
		O1–Cd–N2	95.5(9)
		O2–Cd–N2	159.6(1)
		O4–Cd–N2	96.6(9)
		O3–Cd–N1	162.9(1)
		O1–Cd–N1	111.2(1)
		O2–Cd–N1	90.3(1)
		O4–Cd–N1	87.9(9)
		N2–Cd–N1	72.3(1)

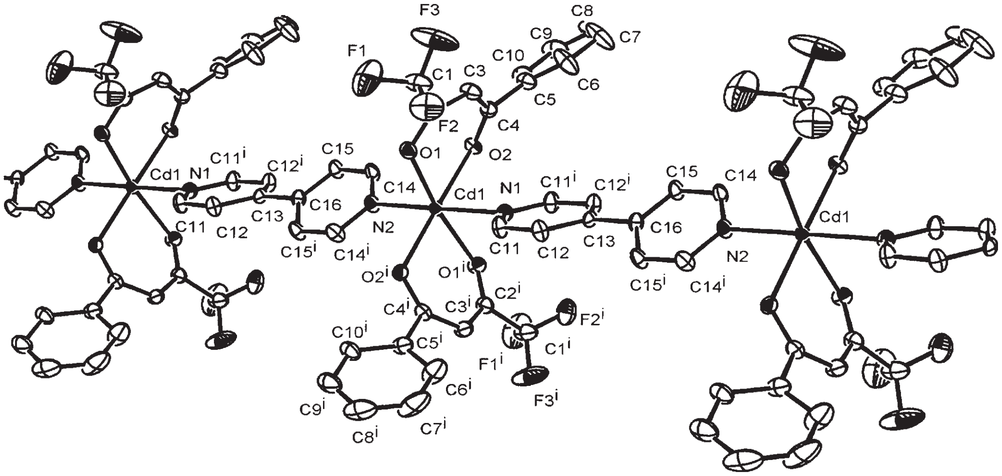


Figure 1. X-ray crystal structure (ORTEP representation) of $[Cd(4,4'\text{-bipy})(TFPB)_2]_n$ (**1**). Ellipsoids 30% probability.

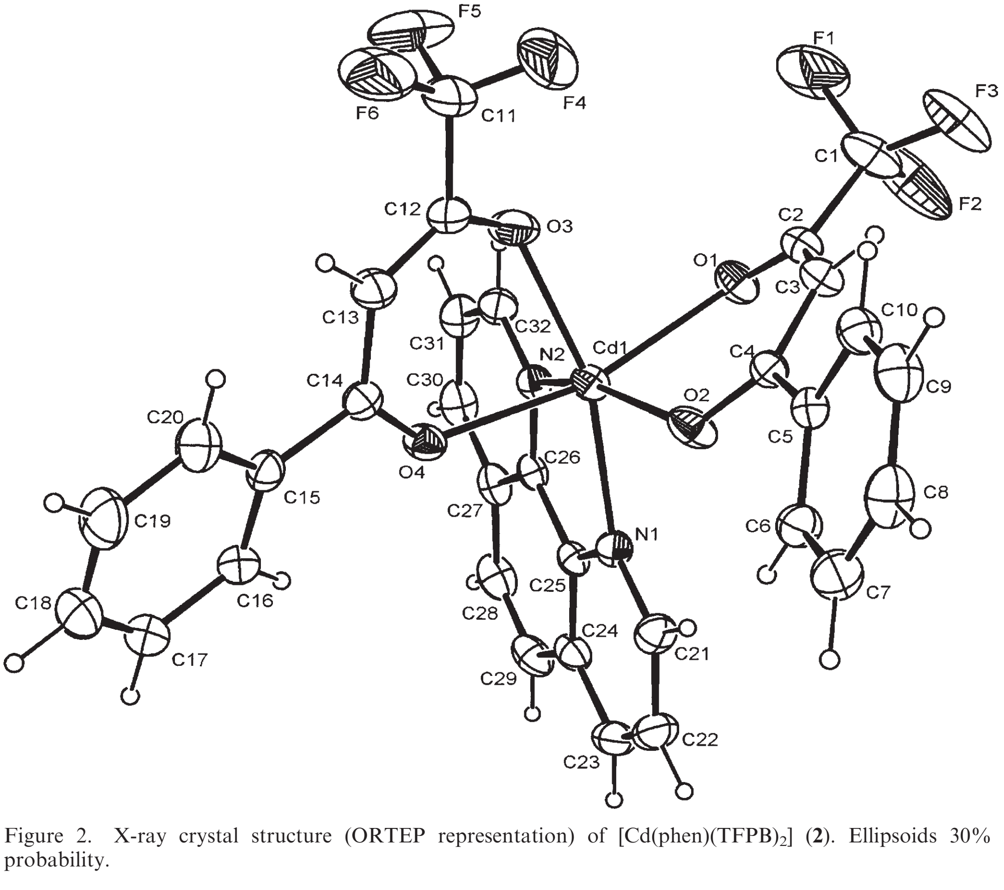


Figure 2. X-ray crystal structure (ORTEP representation) of $[Cd(phen)(TFPB)_2]$ (**2**). Ellipsoids 30% probability.

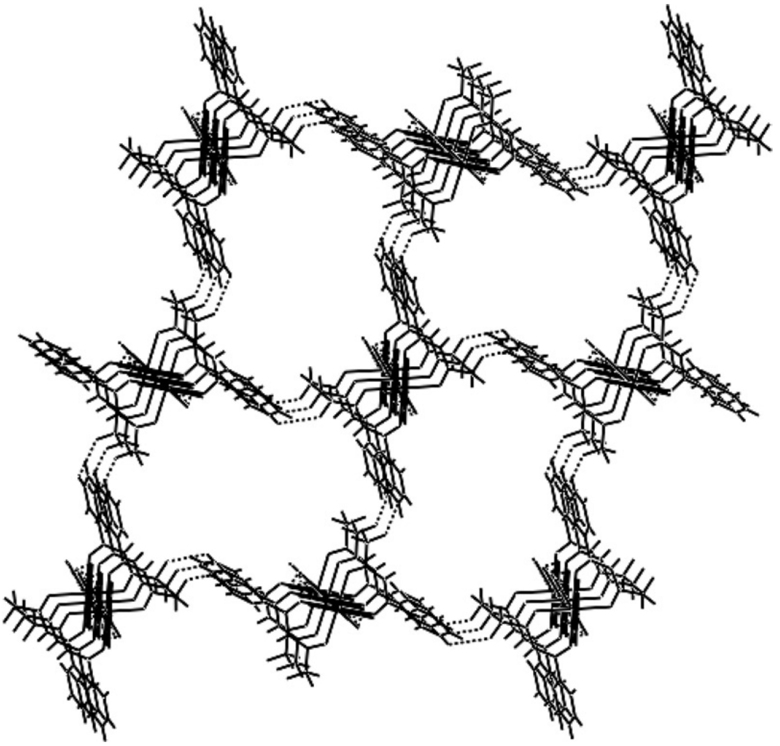


Figure 3. The F···HC interactions in the packing of $[Cd(4,4'\text{-bipy})(TFPB)_2]_n$ (**1**).

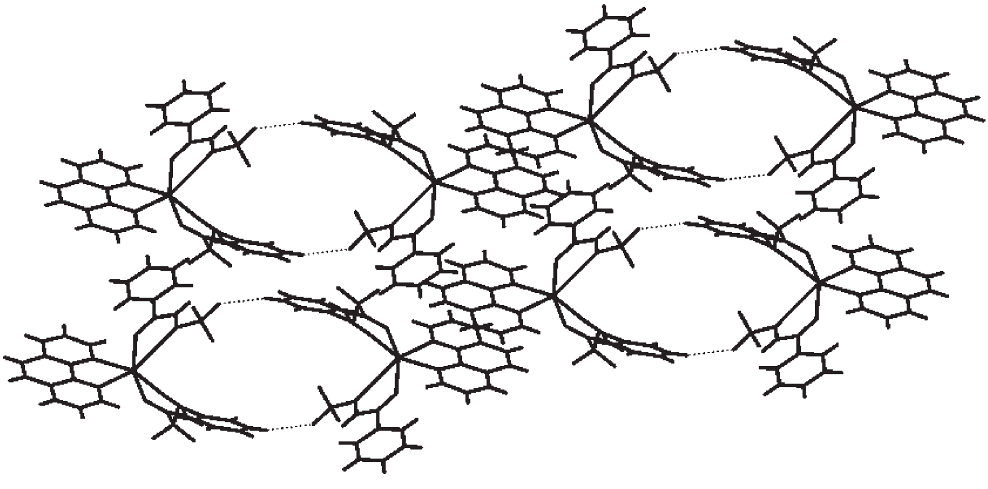


Figure 4. The F···HC interactions in the packing of $[Cd(phen)(TFPB)_2]$ (**2**).

and pyridyl (py) with the distances of $F\cdots H_{ph} = 2.688$ Å $\{C_{ph}\cdots F = 3.34$ Å and $<F\cdots H–C = 125.80^\circ\}$ and $F\cdots H_{py} = 2.75$ Å $\{C_{py}\cdots F = 3.38$ Å and $<F\cdots H–C = 127.46^\circ\}$. In **2** (figure 4), there is one C–H···F–C interaction between fluorine atoms and "ph" hydrogen atoms of $TFPB^-$ with the distance $F\cdots H_{ph} = 2.61$ Å $\{C_{ph}\cdots F = 3.51$ Å and $<F\cdots H–C = 162.04^\circ\}$. In complexes **1–2**

the H···F distances range is 2.566–2.754 Å and the C–H···F angles 125.80–172.40°, values that suggest strong interactions within this class of weak noncovalent contacts [13].

There are π–π stacking interactions between the aromatic rings of adjacent chains in **1** and **2**. In the crystal packing of **1**, the interplanar distance between ''py'' and ''ph'' rings is 3.59 Å and in **2**, the interplanar distance between phen ligands is 3.69 Å. The interplanar distances between aromatic rings in **1** and **2** are normal π–π stacking interactions [14–16].

Thus **1** and **2**, C–H···F–C and π–π stacking interactions control the packing. The obvious question then is whether the C–H···F–C interactions stretch coordinate bonds to result in ligand stacking or whether it is the stacking interaction which has imposed a positioning of the donor atoms for forming the C–H···F–C interactions in the packing. Indeed, it is now realized that C–H···F–C interactions can also play a significant and predictable structure-determining role in the fluorine-substituted β-diketonate metal ion complexes [7–9, 17].

Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallography Data Centre (CCDC) as deposition numbers CCDC-277332 for compound **1** and 277331 for compound **2**. The data can be obtained, free of charge, from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK *via* Fax (+44-1223 336033) or Email (deposit@ccdc.cam.ac.uk).

Acknowledgements

The authors acknowledge financial support by Zanjan and Tarbiat Modarres Universities are gratefully acknowledged.

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