ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 7, pp. 529–536. © Pleiades Publishing, Ltd., 2013.

Manganese(II) and Copper(II) Complexes Based on Pentafluorobenzoate: Interaction of Fluorine in Solid State[1]

C. H. Ge, P. Fan, R. Zhang, J. Liu, F. F. Wang, L. J. Wang, and X. D. Zhang*

College of Chemistry, Liaoning University, Shenyang, 110036 P.R. China

**e-mail: xdzhang@lnu.edu.cn*

Received October 14, 2011

Abstract—The synthesis and characterization of Mn(II) and Cu(II) complexes with the general formula $[Mn(Phen)_2(Pfbz)_2](Hpfbz)$ (**I**) and $[Cu_2(Bipy)_2(Pfbz)_4]$ (**II**) (Phen = 1,10-phenanthroline, Bipy = 2,2'-bipyridine, Pfbz = pentafluorobenzoate) are reported. **I** crystallizes in triclinic crystal system, space group $P\bar{1}$ with $a = 9.755(1)$, $b = 11.302(1)$, $c = 20.064(2)$ Å, $\alpha = 95.799(2)°$, $\beta = 90.176(2)°$, $\gamma = 113.993(2)°$, and $Z = 2$. Complex **II** crystallizes in triclinic crystal system, space group $P\bar{1}$ with $a = 9.661(1)$, $b = 9.951(1)$, $c = 12.891(1)$ Å, $\alpha = 102.943(2)°$, $\beta = 98.972(2)°$, $\gamma = 96.746(2)°$, and $Z = 1$. Of particular interest, intricate C–H···F and F···F interactions in the two crystals play important role in the formation of three dimensional supramolecular networks. F(*lp*)···π (*lp* = lone pair) interaction is recognized in the solid-state structure of **II**.

DOI: 10.1134/S1070328413070014

INTRODUCTION

Non-covalent interactions are omnipresent in supramolecular assemblies, where they often play a crucial role in biology, chemistry, physics, and material [1, 2]. Hydrogen bonding [3–5], π···π interaction [6], O–H···π interaction [7], anion···π interaction [8], cation···π interaction [9], C–H···O interaction [10], lone pair···π interaction [11], X–H···M interaction [12] are common non-covalent bonding interactions which are well accepted in the field of supramolecular chemistry. They are the subjects of many ongoing investigations also today. A recent development of supramolecular chemistry has unearthed many other types of non-covalent forces relating to halogen, which involve strong or weak intermolecular interactions. As important intermolecular linkages, for instance, C–X···CN, C–H···X and X···X interactions have accepted attention in the interpretation and understanding of molecular aggregation in the solid state [13]. Halogen bonding opens up new way for material design and supramolecular synthesis [14]. Though some earlier references do not support that organic fluorine could be able to participate in the formation of non-covalent interactions [15–18]. The ability of organic fluorine to act as participator in weak interaction has been demonstrated extensively both by experimental and by theoretical means [19–24]. There has been a growing interest in such interactions in recent years. This ligand of fluorobenzoate, which can be involving many kinds of weak interaction, has been employed to react with metal ions to form various complexes [25–27]. In this paper, the crystal structures of $[Mn(Phen)_2(Pfbz)_2](Hpfbz)$ (**I**) and $[Cu_2(Bipy)_2(Pfbz)_4]$ (**II**) (Phen = 1,10-phenanthroline, Bipy = 2,2'-bipyridine, Pfbz = pentafluorobenzoate) are reported.

EXPERIMENTAL

All chemicals were of analytical or reagent grade and were used directly without further purification. Elemental analyses were determined on an Elementar Vario EL elemental analyzer. IR spectra were measured as KBr pellets on a Magna-IR 750 spectrophotometer in the 4000–400 cm^{-1} region.

Synthesis of I. Manganese(II) nitrate tetrahydrate (2 mmol), Phen (4 mmol), and pentafluorobenzoic acid (6 mmol) were combined in 30 mL H_2O–ethanol (1 : 1) solution. The mixture was refluxed for 1 h and then cooled to room temperature. To this solution, 1 mL KOH (1 M) was added slowly with continuous stirring. The resulting solution was refluxed for 4 h then allowed to cool to room temperature and then filtered. The filtrate was allowed to slow evaporation at room temperature. By slow evaporation of the solvent, yellow block-shape single crystals suitable for X-ray analysis were obtained within several days. The yield was 27%.

For $C_{45}H_{17}F_{15}N_4O_6Mn$

anal. calcd., %:	C, 51.50;	H, 1.63;	N, 5.34.
Found, %:	C, 51.86;	H, 1.98;	N, 5.81.

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Main IR (KBr; ν, cm^{-1}): 3438 w, 3067 w, 1724 s, 1651 s ν(C=O), 1622 s ν(C=C, C=N), 1517 m, 1496 w, 1484 m, 1430 m, 1383 m, 1360 w, 1321 w, 1236 m, 1101 m, 989 m, 853 w.

Synthesis of II. The preparation of **II** is much similar to the process of **I** with the exception that the primary materials are copper(II) nitrate hydrate (2 mmol), Bipy (2 mmol), and pentafluorobenzoic acid (2 mmol). Crystals were obtained by concentrating. The yield was 35%.

For $C_{48}H_{16}F_{20}N_4O_8Cu_2$

anal. calcd., %:	C, 44.91;	H, 1.26;	N, 4.36.
Found, %:	C, 45.32;	H, 1.69;	N, 4.74.

Main IR (KBr; ν, cm^{-1}): 3073 w, 1677 s ν(C=O), 1598 m ν(C=C, C=N), 1565 w, 1525 m, 1498 m, 1453 m, 1353 m, 1281 m, 1095 w, 990 m, 924 m.

X-ray crystallography. Diffraction data for **I** and **II** were measured on a Bruker SMART CCD diffractometer at 293(2) K using graphite monochromated, MoK_α radiation (λ = 0.71073 Å). The collected data were reduced with the SAINT program [28] and empirical absorption correction was done with the SADABS [29] program. Both structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non–hydrogen atoms [30, 31]. Hydrogen atoms were added geometrically and refined using the riding model.

The summary of the crystal data, experimental details, and refinement results for **I** and **II** are listed in Table 1, while selected bond distances and bond angles are given in Table 2. The atomic coordinates and other parameters of structures **I** and **II** have been deposited with the Cambridge Crystallographic Data Centre (nos. 831003 (**I**) and 831004 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The structure shows that **I** consists of one neutral mononuclear unit and one pentafluorobenzoic acid molecule. As shown in Fig. 1a, the mononuclear unit consists of a manganese ion, two pentafluorobenzoate ligand and two Phen ligand. The coordination environment of metal is that each Mn^{2+} ion is coordinated by four nitrogen atoms (Mn–N 2.260(3)–2.288(3) Å) of two Phen and two oxygen atoms (Mn–O 2.073(2)–2.127(3) Å) from different carboxylate groups, which form an octahedral coordination sphere. The valence angles in the octahedron differ from 90° by a maximum of 17.6° (N(3)Mn(1)N(4) 72.42(9)°). The geometry of the coordination polyhedron about the Mn^{2+} ion causes a significant distortion. The plane of Phen ring (containing N(3), N(4)) is approximately parallel with the plane of benzene ring (defined by C(33)–C(38)) with dihedral angle of 9.1°. Distance between Cg_1 (the centroid of the N(3)/C(13)–C(17) ring) and Cg_2 (the centroid of the C(33)–C(38) ring) is 3.72 Å, which indicates the existence of intra-molecular $\pi\cdots\pi$ interaction. One pentafluorobenzoic acid molecule links pentafluorobenzoate ligand by hydrogen bond (O(5)···O(4) 2.54 Å, O(5)–H(5)···O(4) 166°; symmetry codes: $x - 1, y, z$). Multiple discernible inter-molecular interactions involving fluorine can be observed in the crystal stacking (Fig. 1a). Relative to the non-classic C–H···O hydrogen bond (C(3)···O(2) 3.31 Å, C(3)–H(3)···O(2) 163°; symmetry codes: $x + 1, y, z$), C–H···F and F···F interactions (Table 3, Fig. 2a) play more essential role in the formation of a three dimensional supramolecular network.

Complex **II** is a binuclear compound containing symmetry centers, as shown in Fig. 1b. The asymmetric unit consists of a copper cation in a square-pyramidal arrangement, the base defined by the two nitrogen atoms (N(1) and N(2)) of Bipy molecule and two oxygen atoms (O(2) and O(4) (symmetry code: $-x, -y, -z$)) from a monodentate pentafluorobenzoate and a bridging didentate pentafluorobenzoate (Fig. 1b). This CuO_2N_2 square arrangement is that the mean deviation from the plane is 0.023 Å. The axial site is occupied by one of the pentafluorobenzoate oxygen atoms from a symmetry-related carboxylate ion with Cu–O length of 2.405(2) Å. The angle of Cu–O vector subtending to the plane is 8.23°. The Cu···Cu distance is 3.408 Å. In crystal, there is no classic C–H···O hydrogen bonds (C(18)···O(3) 3.27 Å, C(18)–H(18)···O(3) 153°; symmetry codes: $-1 + x, y, z$; C(21)···O(3) 3.40 Å, C(21)–H(21)···O(3) 159°, symmetry codes: $-1 + x, y, z$; C(22)···O(1) 3.16 Å, C(22)–H(22)···O(1) 135°; symmetry codes: $-x, 2 - y, 2 - z$). Compared with the C–H···O hydrogen bonds, C–H···F and F···F interactions (Table 2, Fig. 2b) are more complex and significant. F(*lp*)···π (F(3)···C(11) 3.03 Å, symmetry codes: $1 - x, 2 - y, 1 - z$; F(2)···C(3) 3.15 Å, symmetry codes: $1 - x, 2 - y, 1 - z$) and C=O(*lp*)···π (O(1)···C(13) 3.06 Å, symmetry codes: $x, 1 + y, z$) interactions are also found (Fig. 3) [32, 33]. An intricate three-dimensional non-covalent network was generated based on above mentioned interactions.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (nos. 20971062/B010303 and 21171081/B0103), Natural Science Foundation of Liaoning Province (no. 201202093)

Table 1. Crystallographic data and details of the experiment and refinement for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	1049.57	1283.75
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.7550(11)	9.6605(11)
b, Å	11.3016(13)	9.9510(11)
c, Å	20.064(2)	12.8914(14)
α, deg	95.799(2)	102.943(2)
β, deg	90.176(2)	98.972(2)
γ, deg	113.993(2)	96.746(2)
V, Å^3	2008.1(4)	1178.0(2)
Z	2	1
ρ_{calcd}, g cm^{-3}	1.736	1.810
μ, mm^{-1}	0.458	1.043
$F(000)$	1046	634
Crystal size, mm	0.23 × 0.18 × 0.17	0.30 × 0.26 × 0.21
θ Range for data collection, deg	1.98–25.00	2.13–25.00
Index ranges	$-7 \le h \le 11$, $-13 \le k \le 13$, $-23 \le l \le 23$	$-11 \le h \le 11$, $-11 \le k \le 11$, $-12 \le l \le 15$
Reflections collected	10674	6109
Independent reflections (R_{int})	7037 (0.0822)	4144 (0.0200)
Reflections observed ($I > 2\sigma(I)$)	4868	3176
T_{min}, T_{max} transmission factors	0.911, 0.931	0.751, 0.812
Refined parameters	641	370
Goodness-of-fit on F^2	0.950	1.061
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0618$, $wR_2 = 0.1536$	$R_1 = 0.0412$, $wR_2 = 0.0968$
R indices (all data)	$R_1 = 0.0843$, $wR_2 = 0.1654$	$R_1 = 0.0589$, $wR_2 = 0.1040$
Largest diff. peak and hole, e Å^{-3}	0.489 and –0.510	0.320 and –0.367

Table 2. Selected bond lengths and angles in **I** and **II**

I				**II**			
Bond	d, Å	Bond	d, Å	Bond	d, Å	Bond	d, Å
Mn(1)–O(1)	2.073(2)	Mn(1)–N(2)	2.283(3)	Cu(1)–O(2)	1.938(2)	Cu(1)–N(2)	2.003(2)
Mn(1)–O(3)	2.127(3)	Mn(1)–N(3)	2.286(2)	Cu(1)–O(4)	1.973(2)	Cu(1)–O(4)	2.405(2)
Mn(1)–N(1)	2.260(3)	Mn(1)–N(4)	2.288(3)	Cu(1)–N(1)	2.002(2)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Mn(1)O(3)	96.97(10)	N(1)Mn(1)N(3)	162.22(10)	O(2)Cu(1)O(4)	89.75(9)	N(1)Cu(1)N(2)	80.63(10)
O(1)Mn(1)N(1)	102.96(10)	N(2)Mn(1)N(3)	93.81(9)	O(2)Cu(1)N(1)	93.78(10)	O(2)Cu(1)O(4)	87.68(8)
O(3)Mn(1)N(1)	86.88(10)	O(1)Mn(1)N(4)	160.43(10)	O(4)Cu(1)N(1)	175.90(9)	O(4)Cu(1)O(4)	78.22(8)
O(1)Mn(1)N(2)	86.78(11)	O(3)Mn(1)N(4)	88.14(10)	O(2)Cu(1)N(2)	173.15(9)	N(1)Cu(1)O(4)	103.99(9)
O(3)Mn(1)N(2)	160.06(9)	N(1)Mn(1)N(4)	96.15(9)	O(4)Cu(1)N(2)	95.70(9)	N(2)Cu(1)O(4)	97.48(9)
N(1)Mn(1)N(2)	73.20(10)	N(2)Mn(1)N(4)	94.84(10)				
O(1)Mn(1)N(3)	88.01(10)	N(3)Mn(1)N(4)	72.42(9)				
O(3)Mn(1)N(3)	105.86(9)						

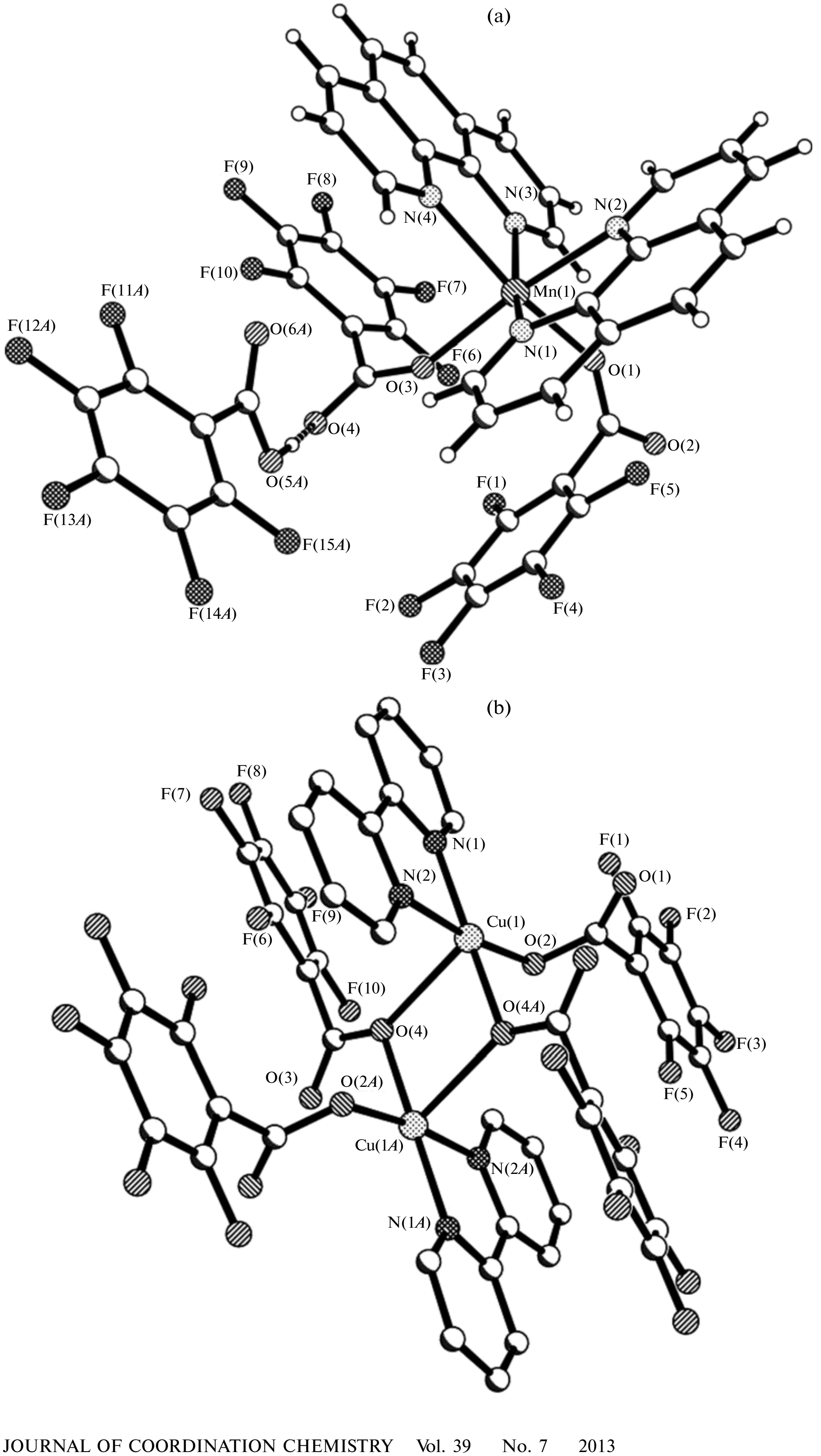
Table 3. C–H···F and F···F interactions of **I** and **II**

C–H···F	Distance, Å			Angle D–H···A, deg	Symmetry
	D–H	H···A	D···A		
I					
C(24)–H(24)···F(7)	0.93	2.45	3.27	147	$1 + x, y, z$
C(14)–H(14)···F(2)	0.93	2.62	3.20	122	$x, 1 + y, z$
C(10)–H(10)···F(5)	0.93	2.55	3.18	125	$2 - x, 2 - y, 1 - z$
C(20)–H(20)···F(11)	0.93	2.63	3.33	133	$1 - x, 2 - y, 2 - z$
C(22)–H(22)···F(10)	0.93	2.65	3.551	163	$2 - x, 2 - y, 2 - z$
C(23)–H(23)···F(8)	0.93	2.56	3.46	161	$1 + x, y, z$
C(23)–H(23)···F(9)	0.93	2.61	3.33	134	$2 - x, 2 - y, 2 - z$
II					
C(23)–H(23)···F(2)	0.93	2.60	3.27	130	$x, y, 1 + z$
C(12)–H(12)···F(2)	0.93	2.67	3.22	119	$1 - x, 2 - y, 1 - z$
C(16)–H(16)···F(8)	0.93	2.57	3.42	151	$-x, 1 - y, 1 - z$

F···F	Distance, Å	Symmetry
	D···D	
I		
F(2)···F(14)	2.89	x, y, z
F(8)···F(9)	2.79	$1 - x, 2 - y, 2 - z$
F(12)···F(12)	2.88	$1 - x, 1 - y, 2 - z$
II		
F(4)···F(7)	2.94	$1 + x, 1 + y, z$
F(3)···F(9)	2.85	$1 - x, 2 - y, 1 - z$

→

Fig. 1. The molecular structures of **I** (a) and **II** (b), showing the atom-numbering scheme. In complex **I**, the O–H···O hydrogen bond is indicated as dotted line.


(a)
F(9)
F(8)
N(4)
N(3)
N(2)
F(10)
F(7)
Mn(1)
F(11A)
F(12A)
O(6A)
N(1)
F(6)
O(3)
O(1)
O(4)
O(2)
O(5A)
F(1)
F(5)
F(13A)
F(15A)
F(2)
F(4)
F(14A)
F(3)
(b)
F(8)
F(7)
N(1)
F(1)
O(1)
N(2)
F(2)
F(9)
Cu(1)
F(6)
O(2)
F(10)
O(4A)
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N(2A)
N(1A)

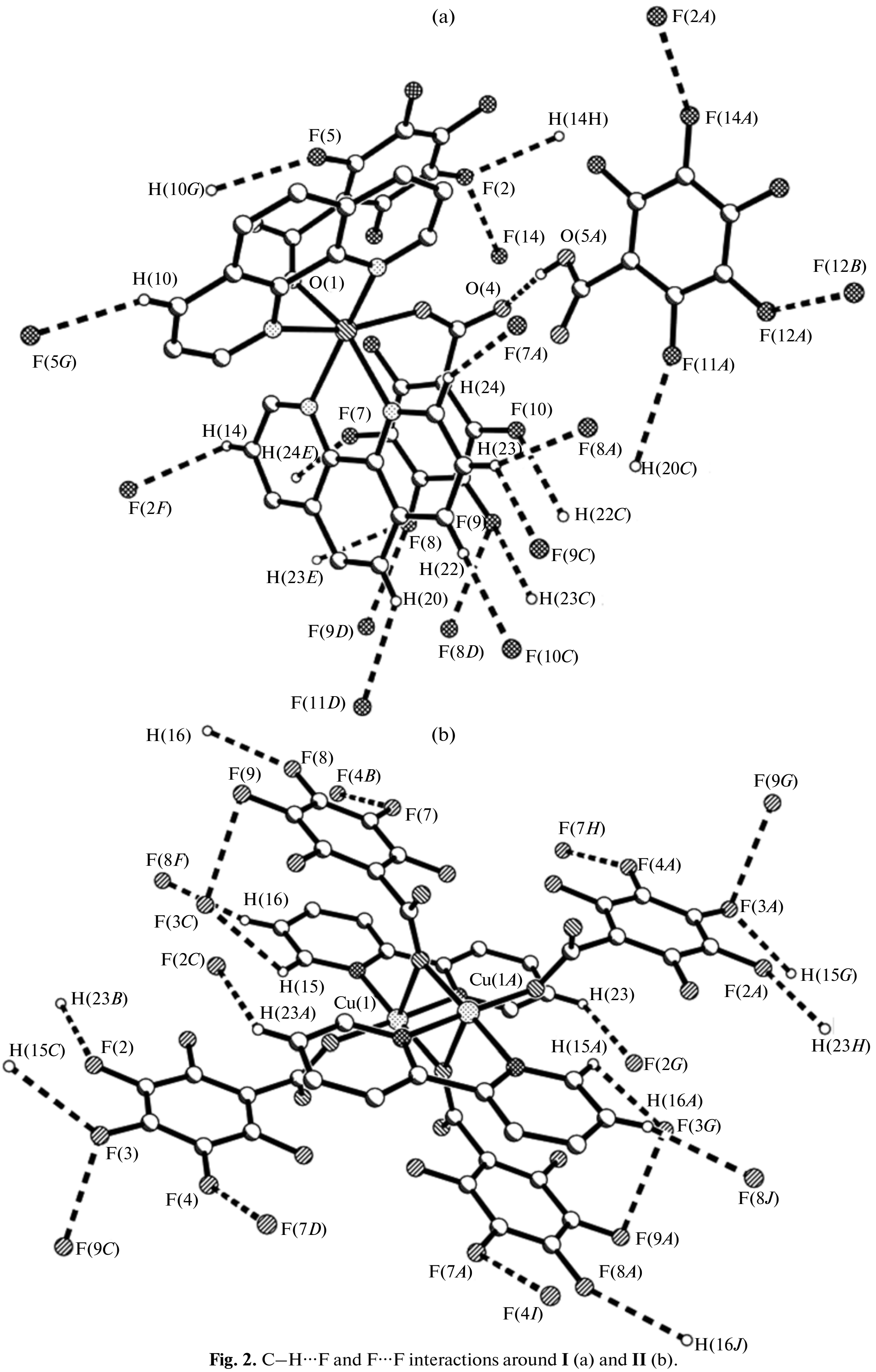
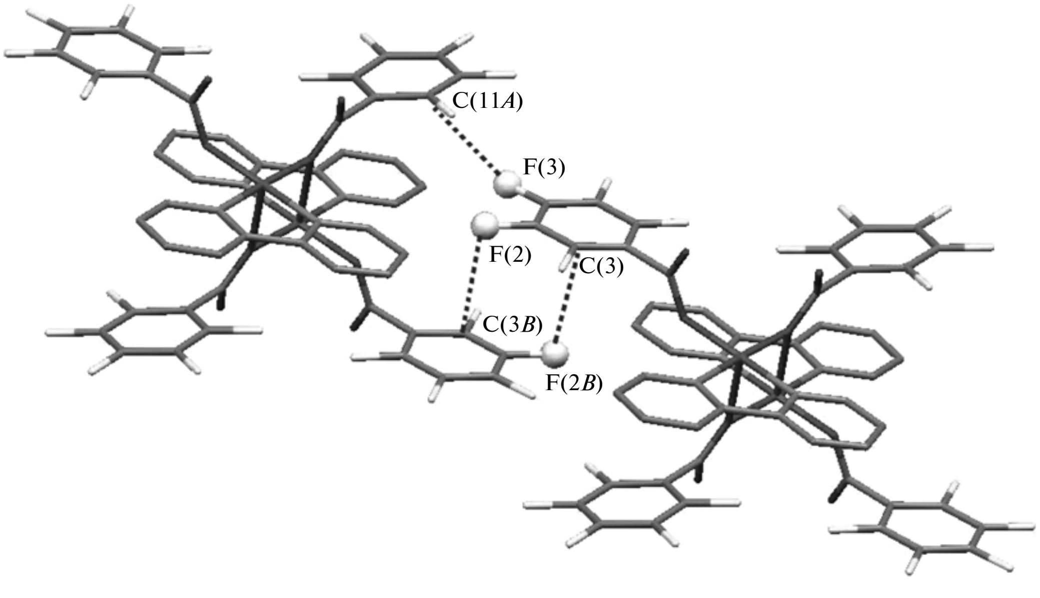


Fig. 2. C–H···F and F···F interactions around **I** (a) and **II** (b).



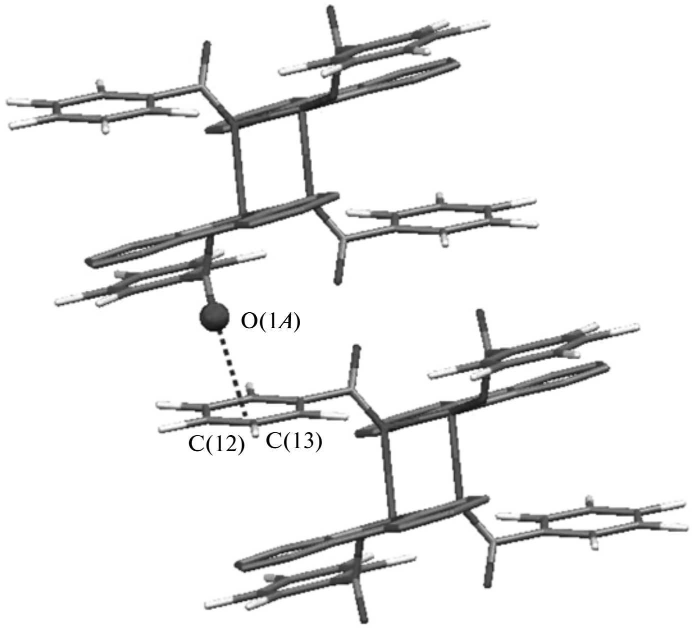


Fig. 3. F(*lp*)···π (top) and C=O(*lp*)···π (bottom) interactions in crystal of **II**.

and Liaoning Provincial Department of education innovation team projects (no. LT2012001).

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