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Synthesis and Structural Characterization of Two Copper Complexes with Long Rigid Ligands[1]

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Abstract—Two copper complexes with long rigid ligands, $Cu(Tta)_2(L^1)$ (**I**), and $Cu(Tta)_2(L^2)$ (**II**), where L^1 = (*E*)-3-(4-(1*H*-benzo[d]imidazol-1-yl)-(4-phenyl)phenyl)-1-phenylprop-2-en-1-one, L^2 = (*E*)-3-(4-(1*H*-imidazol-1-yl)phenyl)-1-(4-phenyl)phenyl)prop-2-en-1-one), have been synthesized and characterized. The single-crystal X-ray analysis (CIF files CCDC nos. 1409671 (**I**) and 1409672 (**II**)) for complexes **I** and **II** demonstrates that each copper ion assumes a distorted square-pyramidal MO_4N polyhedron in which four oxygen atoms come from the Tta ligands, and one nitrogen atom comes from the N-donor ligand. Both of the complexes are linked into 3D networks through weak intermolecular interactions.

Keywords: N-donor ligand, copper complex, crystal structure, coordination compound, hydrogen bond

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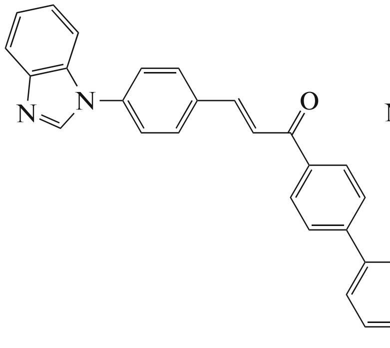
INTRODUCTION

In the past decades, the fluorinated β-diketonate complexes and their derivatives have received much attention due to their potential applications for new inorganic materials as well as their fascinating geometric aspects [1–6]. An effective and facile method for the synthesis of these complexes is still the appropriate choice of well-designed organic ligands with the copper precursors [1–9]. Among various organic ligands, compounds with N-donor heterocycles are often selected as multifunctional organic linkers because of their unique ability of coordinating to metal ions [1–10].

Recently, we have reported a few copper complexes with N-donor ligands [8–10]. As part of our research on the Tta-containing copper(II) complexes, we investigated the copper complexes with long rigid ligands, $Cu(Tta)_2(L^1)$ (**I**), and $Cu(Tta)_2(L^2)$ (**II**), (L^1 = (*E*)-3-(4-(1*H*-benzo[d]imidazol-1-yl)-(4-phenyl)phenyl)-1-phenylprop-2-en-1-one, L^2 = (*E*)-3-(4-(1*H*-imidazol-1-yl)phenyl)-1-(4-phenyl)phenyl)prop-2-en-1-one).



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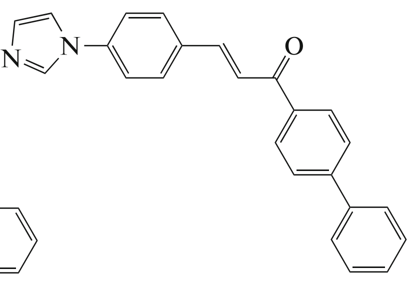

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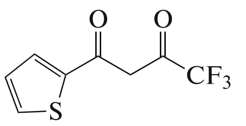

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EXPERIMENTAL

Materials and measurements. All reagents were purchased as analytical grade and used without further purification. Cu(Tta)$_2$, 4-imidazolylbenzaldehyde and 4-(1*H*-benzo[d]imidazol-1-yl)benzaldehyde were synthesized according to the literature method [11, 12]. Elemental analyses (C, H, N) were performed in an Elementar vario EL cube elemental analyzer. IR spectrum was recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region.

Synthesis of L^1. A methanolic sodium hydroxide solution (40%, 10 mmol) was added dropwise to a methanol solution of 4-(1*H*-imidazol-1-yl)benzaldehyde (11 mol), 4-phenylacetophenone (10 mmol) over a period of 24 h with continuous stirring till completion of reaction (as indicated by TLC). Precipitates obtained were filtered and washed with cold methanol–water mixture (1 : 10). Finally, the product was recrystallized from methanol. The yield was 92%.

IR (KBr; ν, cm^{-1}): 3059, 1657, 1599, 1570, 1518, 1490, 1454, 1424, 1402, 1333, 1283, 1219, 1183, 1011, 977, 825, 768, 743, 694, 619, 575, 527, 487, 427.

For $C_{28}H_{20}N_2O$

anal. calcd., %:	C, 83.98;	H, 5.03;	N, 7.00.
Found, %:	C, 83.84;	H, 4.90;	N, 6.91.

Synthesis of L^2. The compound was obtained as a pale yellow solid using the same procedure as for L^1 by replacing 4-(1*H*-benzo[d]imidazol-1-yl)benzaldehyde with 4-(1*H*-imidazol-1-yl)benzaldehyde. The yield was 94%.

IR (KBr; ν, cm^{-1}): 3099, 1659, 1599, 1577, 1522, 1487, 1449, 1425, 1404, 1365, 1337, 1317, 1302, 1270, 1254, 1225, 1207, 1185, 1128, 1105, 1057, 1034, 1007, 980, 959, 905, 874, 844, 824, 771, 741, 720, 690, 657, 617, 536, 514, 476, 444.

For $C_{24}H_{18}N_2O$

anal. calcd., %:	C, 82.26;	H, 5.18;	N, 7.99.
Found, %:	C, 82.17;	H, 5.11;	N, 7.93.

Synthesis of I. To a CH_2Cl_2 solution (20 mL) of Cu(Tta)$_2$ (124.5 mg, 0.25 mmol), L^1 (100.2 mg, 0.25 mmol) in CH_2Cl_2 was added slowly. The mixture was stirred for 2 h and the resulting light green solution filtrated was kept at room temperature for several days. Green crystals, suitable for X-ray crystallography, formed upon evaporation of the solvent. The yield was 176.7 mg (78%).

IR (KBr; ν, cm^{-1}): 3082, 1664, 1591, 1539, 1516, 1456, 1410, 1357, 1315, 1253, 1231, 1190, 1142, 1063, 1029, 1011, 978, 937, 862, 824, 785, 746, 692, 623, 590, 576, 530, 489, 465, 430.

For $C_{44}H_{28}F_6N_2O_5S_2Cu$

anal. calcd., %:	C, 58.31;	H, 3.11;	N, 3.09.
Found, %:	C, 58.22;	H, 2.99;	N, 3.13.

Synthesis of II. The compound was obtained as a white solid solid using the same procedure as for **I** by replacing 4-(1*H*-benzo[d]imidazol-1-yl)benzaldehyde with 4-(1*H*-imidazol-1-yl)benzaldehyde. The yield was 154.0 mg (72%).

IR (KBr; ν, cm^{-1}): 3124, 1661, 1597, 1555, 1437, 1414, 1353, 1313, 1256, 1231, 1189, 1144, 1066, 1033, 877, 825, 787, 743, 715, 690, 648, 619, 527.

For $C_{40}H_{26}F_6N_2O_5S_2Cu$

anal. calcd., %:	C, 56.10;	H, 3.06;	N, 3.27.
Found, %:	C, 56.01;	H, 2.82;	N, 3.15.

X-ray crystallographic studies. All data were collected on an Agilent Technology SuperNova Eos Dual system with a (MoK_α, λ = 0.71073 Å) micro focus source and focusing multilayer mirror optics. The data were collected at a temperature of 293 K and processed using CrysAlis$^{\text{Pro}}$ [13]. The structures were solved and refined using full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97 [14]. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms of the ligands were localized in their calculated positions and refined using a riding model. The details of crystal data and refinement for **I** and **II** are given in Table 1, while the selected bond lengths and angles are listed in Table 2.

Supplementary material for structures **I**, **II** has been deposited with the Cambridge Crystallographic Data Centre (nos. 1409671 and 1409672, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Two ligands were synthesized as pale yellow solids under mild conditions. They were characterized through spectroscopic techniques along with their elemental analyses which were found in accordance with the calculated values. Compounds **I** and **II** were prepared cleanly as green crystalline products via the combination of the ligand and Cu(Tta)$_2$. Both **I** and **II** are air stable and soluble in common organic solvents such as acetonitrile, acetone, alcohol, and dichloromethane. The infrared spectra of **I** and **II** were fully consistent with their formulations. The IR spectra showed characteristic band corresponding to enolized 1,3-dicarbonyl stretching frequencies at ~1660 cm^{-1} (1664 for **I**, 1661 cm^{-1} for **II**) and sharp C–F deforma-

Table 1. Crystallographic characteristics and the X-ray-data collection and structure-refinement parameters for **I** and **II**

Temperature, K	293(2)	293(2)
Fw	906.37	856.29
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal size, mm	0.25 × 0.22 × 0.21	0.24 × 0.22 × 0.20
a, Å	10.2113(3)	9.8244(4)
b, Å	10.6392(4)	10.0622(4)
c, Å	20.0474(7)	20.6739(8)
α, deg	75.948(3)	89.604(3)
β, deg	78.415(2)	89.728(3)
γ, deg	84.199(2)	70.850(4)
V, Å^3	2066.60(12)	1930.57(13)
Z	2	2
ρ_{cacld}, g cm^{-3}	1.457	1.473
μ, mm^{-1}	0.704	0.749
θ Range, deg	2.94–25.50	2.90–25.50
Reflections measured/unique (R_{int})	14480/7672 (0.0258)	17055/7163 (0.0247)
Reflections with $I > 2\sigma(I)$	5255	5682
Data/restraints/parameters	7672/0/541	7163/1/505
GOOF on F^2	1.027	1.014
R_1/wR_2 ($I > 2\sigma(I)$)	0.0628, 0.1489	0.0570, 0.1466
R_1/wR_2 (all data)	0.0947, 0.1649	0.0703, 0.1551
$\Delta\rho_{\max}/\Delta\rho_{\min}$, e/Å^3	0.565/–0.330	0.948/–0.422

tion frequencies at ~1440 cm^{-1} (1437 and 1456 cm^{-1} for **I** and **II**, respectively).

The molecular structure of complexes **I** and **II** is presented in Fig. 1. In molecules of **I**, the Cu^{2+} ion is penta-coordinated by four oxygen atoms of two Tta ligands and one nitrogen atom of ligand L^1, in which the distorted coordination polyhedron is close to a square pyramid with $s = 0.04$ [15]. The apical site of the square pyramid is occupied by N(1) of L^1 ligand. The Cu–N (2.255(4) Å) distances are much longer than Cu–O (1.932(3), 1.933(3), 1.934(3), 1.941(3) Å) distances. The Tta fragments *cis* to each other forms two M–O–C–C–C–O six-membered chelate rings, and the metal lies deviating from this calculated plane with 0.02 and 0.21 Å, respectively. The copper atom is shifted by 0.14 Å towards N(1) from the basal plane which itself forms an interplanar angle of 74° with the benzimidazole ring of L^1.

The central Cu^{2+} ion in **II** is also penta-coordinated with a distorted coordination polyhedron, in which the coordination around the Cu(II) center is achieved by the four oxygen atoms of two Tta ligands and one nitrogen atom of the L^2 ligand. However, the equatorial plane is formed by one nitrogen atoms of the L^2

Table 2. Selected bond distances (Å) and bond angles (deg) for **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(2)	1.932(3)	Cu(1)–O(2)	1.944(2)
Cu(1)–O(3)	1.933(3)	Cu(1)–O(4)	1.957(2)
Cu(1)–O(4)	1.934(3)	Cu(1)–O(1)	1.970(2)
Cu(1)–O(1)	1.941(3)	Cu(1)–N(1)	2.000(3)
Cu(1)–N(1)	2.255(4)	Cu(1)–O(3)	2.178(3)
Angle	ω, deg	Angle	ω, deg
O(2)Cu(1)O(3)	169.92(12)	O(2)Cu(1)O(4)	176.84(10)
O(2)Cu(1)O(4)	83.58(12)	O(2)Cu(1)O(1)	91.79(10)
O(3)Cu(1)O(4)	92.70(11)	O(4)Cu(1)O(1)	89.37(10)
O(2)Cu(1)O(1)	92.59(12)	O(2)Cu(1)N(1)	88.96(11)
O(3)Cu(1)O(1)	89.94(11)	O(4)Cu(1)N(1)	88.99(11)
O(4)Cu(1)O(1)	172.22(12)	O(1)Cu(1)N(1)	160.95(12)
O(2)Cu(1)N(1)	92.42(13)	O(2)Cu(1)O(3)	95.63(10)
O(3)Cu(1)N(1)	96.96(13)	O(4)Cu(1)O(3)	87.29(10)
O(4)Cu(1)N(1)	90.08(13)	O(1)Cu(1)O(3)	90.76(11)
O(1)Cu(1)N(1)	96.87(13)	N(1)Cu(1)O(3)	108.12(11)
C(38)N(1)C(39)	105.0(4)	C(38)N(1)C(39)	105.7(3)
C(38)N(1)Cu(1)	121.8(3)	C(38)N(1)Cu(1)	124.6(2)
C(39)N(1)Cu(1)	130.4(3)	C(39)N(1)Cu(1)	129.3(2)
C(38)N(2)C(40)	105.3(4)	C(38)N(2)C(40)	106.8(3)
C(38)N(2)C(35)	125.0(4)	C(38)N(2)C(35)	125.4(3)
C(40)N(2)C(35)	129.5(4)	C(40)N(2)C(35)	127.8(3)
C(2)O(1)Cu(1)	122.8(3)	C(2)O(1)Cu(1)	122.6(2)
C(4)O(2)Cu(1)	127.9(3)	C(4)O(2)Cu(1)	126.3(2)
C(10)O(3)Cu(1)	122.6(3)	C(10)O(3)Cu(1)	118.8(2)
C(12)O(4)Cu(1)	127.1(3)	C(12)O(4)Cu(1)	127.4(2)

Table 3. Intra- and intermolecular interaction for **I** and **II***

D–H···A	Distance, Å			Angle DHA, deg	Symmetry codes
	D–H	H···A	D···A		
I					
C(3)–H(3)···F(3)	0.93	2.40	2.754(6)	102	
C(11)–H(11)···F(4)	0.93	2.35	2.716(6)	103	
C(31)–H(31)···O(5)	0.93	2.50	2.812(6)	100	
C(41)–H(41)···O(5)	0.93	2.47	3.220(7)	138	$1 - x, 1 - y, 1 - z$
F(1)···S(2)			3.194(6)		$x, y + 1, z$
II					
C(3)–H(3)···F(2)	0.93	2.36	2.722(5)	103	
C(11)–H(11)···F(5)	0.93	2.40	2.742(6)	102	
C(30)–H(30)···O(3)	0.93	2.56	3.480(5)	170	$x - 1, y, z$
C(31)–H(31)···O(5)	0.93	2.53	2.835(6)	100	
C(37)–H(37)···O(3)	0.93	2.41	3.325(5)	167	$x - 1, y, z$
C(38)–H(38)···O(4)	0.93	2.39	2.849(4)	110	
C(40)–H(40)···O(5)	0.93	2.60	3.493(5)	161	$-x, 1 - y, 2 - y$
C(21)–H(21)···*Cg*(1)	0.93	2.94	3.739(6)	145	$x - 1, y, z$
Cg···*Cg*	*d*, Å		Dihedral angle, deg		
*Cg*1···*Cg*2	3.830(8)		9		$x, y - 1, z$
*Cg*1···*Cg*1	3.635(7)		0		$1 - x, 1 - y, 1 - z$

* *Cg*1, *Cg*2 are centroids of C(23)–C(28) and C(38)–N(1)–C(39)–C(40)–N(2), respectively, for **I**; *Cg*1 is centroids of S(2)–C(13)–C(16) for **II**.

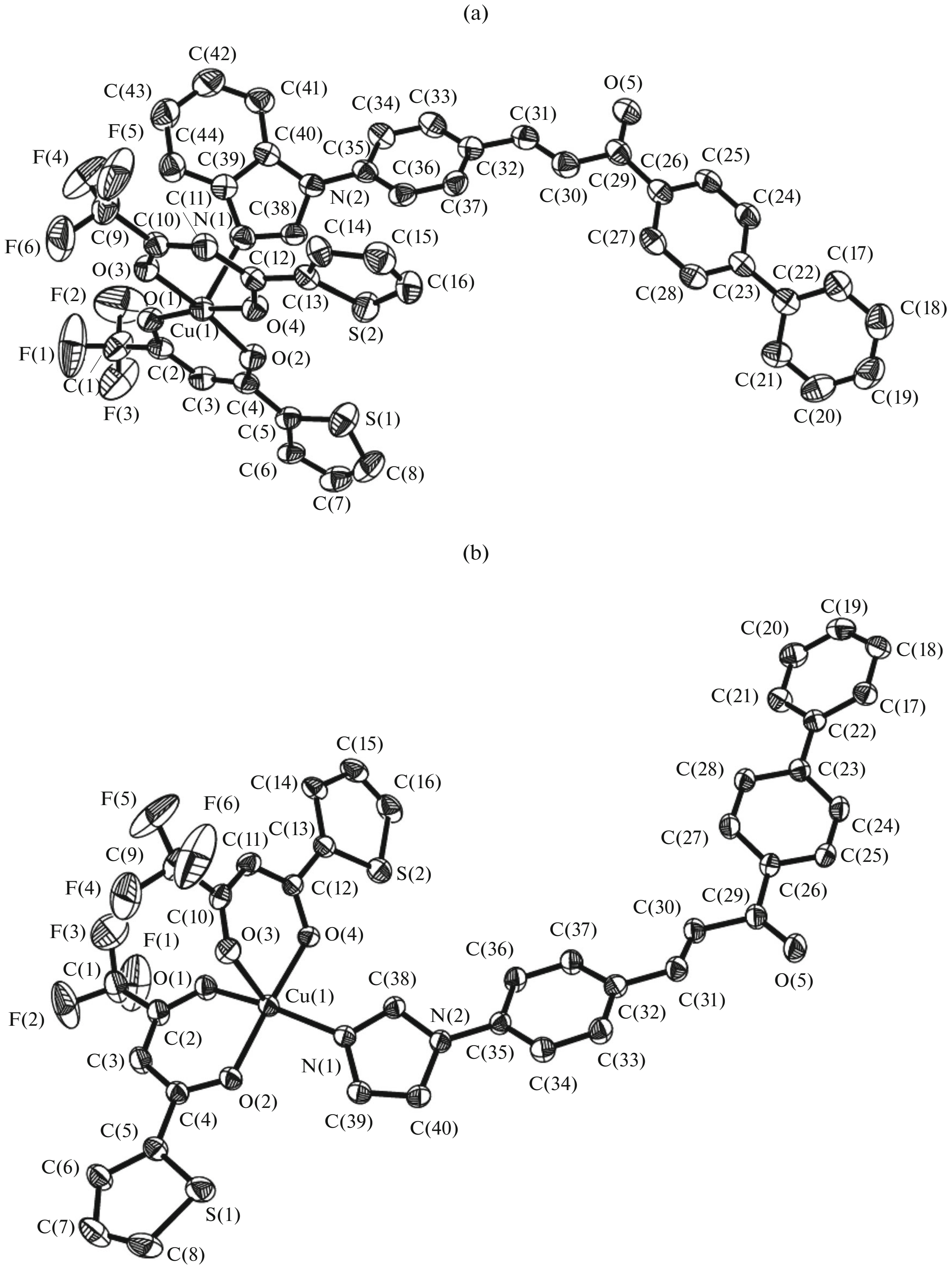

Fig. 1. Molecular structure of complex **I** (a) and **II** (b) showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

ligand, three tta oxygen atoms O(1), O(2), and O(4) (deviation of Cu(1) by 0.187 Å towards plane defined by O(1), O(2), O(4) and N(1)), which is different from that of complex **I**. The Cu(1)–O(Tta) and Cu(1)–N(1) bond lengths in the equatorial sites are in the 1.944(2)–2.000(3) Å range, while the Cu(1)–O(3) bond length in the apical site is 2.178(3) Å, much longer than the equatorial those in the equatorial sites.

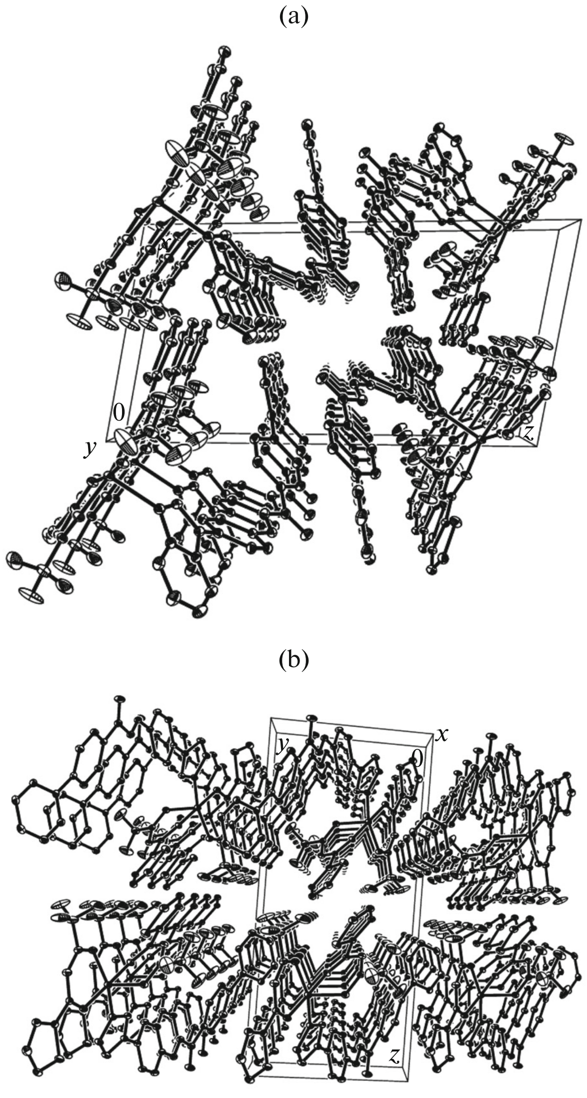

Fig. 2. Packing diagram of **I** view down the *y* axis (a) and **II** view down the *x* axis.

In the solid state, the complex **I** interact one with the others through C(3)–H(3)···F(3), C(11)–H(11)···F(4), C(31)–H(31)···O(5), C(41)–H(41)···O(5) hydrogen bonds, weak π···π interactions and S···F van der Waals interactions (Table 3, Fig. 2a). In complex **II**, intermolecular hydrogen bonds, C–H···π and π···π interactions are the important factors in governing the solid-state arrangement (Table 3, Fig. 2b).

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