Spectroscopic, Thermal, and Structural Studies of Two New Co-Crystals of [4,4′-Bithiazole]-2,2′-diamine

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Two new 2:1 co-crystals based on [4,4′-bithiazole]-2,2′-diamine (=2,2′-diamino-4,4′-bithiazole (DABTZ)) with 2,2′-bipyridine (bipy) and benzo-18-crown-6 (bk) were synthesized by slow-evaporation method in MeOH. These co-crystals were characterized by means of elemental analysis, and IR, and ^{1}H- and ^{13}C-NMR spectroscopy. Also, thermal analyses under air atmosphere and X-ray crystallography have been performed on these structures. X-Ray single-crystal analyses revealed that these networks contain large vacant voids. These structures, [(DABTZ)$_2$(bipy)] and [(DABTZ)$_2$(bk)(MeOH)], crystallized in monoclinic and triclinic forms with space groups of $P2_1/c$ and $P\bar{1}$, respectively. The self-assembly of these compounds in the solid state is likely caused by both H-bonding and π–π stacking.

Introduction. – The term 'co-crystal' describes the crystal structures that contain a selected species plus some other molecular component. This phenomenon is an important tool to the crystal engineer, because it allows a molecule to be studied in different solid-state environments where each structure will have distinctive physical characteristics and unique nonbonded interactions. The co-crystallization reactions provide helpful means for probing the importance and balance between different intermolecular interactions and, thus offer practical guidelines for developing new methodologies in supramolecular synthesis. The H-Bonding as the strongest intermolecular contact has been studied for many decades. There has been a substantial increase in the use of H-bonds as design elements in organic solids [1–6]. Determination of the structures of co-crystals from [4,4′-bithiazole]-2,2′-diamine (DABTZ) with 2,2′-bipyridine (bipy) and benzo-18-crown-6 (bk) provide novel supramolecular compounds involving NH···O and NH···N H-bonding, and π–π stacking interactions. These interactions between the py groups of bipy molecules in [(DABTZ)$_2$(bipy)] are of the face-to-face 'π-stacking' type [7–10].

Results and Discussion. – The IR spectrum of the compounds shows absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1600-cm^{-1} range. The absorption bands of the NH$_2$ groups are observed as strong bands centered at 3075 and 3260 cm^{-1} for [(DABTZ)$_2$(bipy)], as well as at 3090 and 3215 cm^{-1} for [(DABTZ)$_2$(bk)(MeOH)], and are significantly shifted to the lower-frequency region, compared to the only 'DABTZ' (3270 and 3430 cm^{-1}). The relatively low frequency of the band is indicative of H-bonding. The relatively weak absorption band at 2900 cm^{-1}

is due to the C–H modes involving the –CH_2– in the [$(DABTZ)_2$(bk)(MeOH)]. Bands in the region of 550–1070 cm^{-1} are due to the bending vibration of C–H group in or out of the aromatic plane, and ring deformation absorptions of py in [$(DABTZ)_2$(bipy)] and ph in [$(DABTZ)_2$(bk)(MeOH)] molecules. There are no differences between the ^{1}H- and ^{13}C-NMR spectra of co-crystal and of the individual components. In other words, the co-crystals disintegrate in DMSO as strong H-bonding acceptors. The thermal decomposition behavior of [$(DABTZ)_2$(bk)(MeOH)] was investigated in static air atmosphere from ambient temperature to 700° (*Fig. 1*). This compound is stable up to 110°, and releases one MeOH molecule up to 115° with one endothermic feature at 117° (obs. 4.10%, calc. 4.30%) to give the MeOH-free product [$(DABTZ)_2$(bk)], which is stable up to 210°. The weight loss of 54.10% from 210 to 425° is equivalent to the loss of two DABTZ molecules (calc. 53.15%) with two exothermic events at 270 and 350°. Decomposion of the bk molecule takes place at 430.60°, and the experimental mass loss of 40.50% is consistent with the calculated value 41.90% for the elimination of one bk molecule with an exothermic feature at 465°. X-Ray single-crystal analysis revealed that compounds [$(DABTZ)_2$(bipy)] and [$(DABTZ)_2$(bk)(MeOH)] crystallize in monoclinic and triclinic form with space groups of $P2_1/c$ and P_1, respectively (*Table 1*). Also, the X-ray single-crystal analysis demonstrated that, in the solid state, the DABTZ moieties are connected through self-complementary H-bonds, as well as in a N–H···N H-bond involving one H-atom of the amine moiety (the H-bond donor) and a N-atom of DABTZ (the H-bond acceptor). The other amine H-atom acts as the H-bond donor with a N-atom of 2,2′-bipyridine and benzo-18-crown-6 ligands as the H-bond acceptor (*Tables 2* and *3*). Consequently, the self-complementary H-bonds system grows into a two-dimensional network by packing *via* the H-bonding interactions (*Figs. 2* and *3*). The DABTZ molecules in the compounds [$(DABTZ)_2$(bipy)] and [$(DABTZ)_2$(bk)(MeOH)] lies in the inversion center with the symmetry transformation code $-x$, $-y$, $-z$. In [$(DABTZ)_2$(bipy)], the aromatic rings of bipy are not coplanar, but the aromatic rings of 'DABTZ' are coplanar, because the dihedral angle between the two rings within bipy

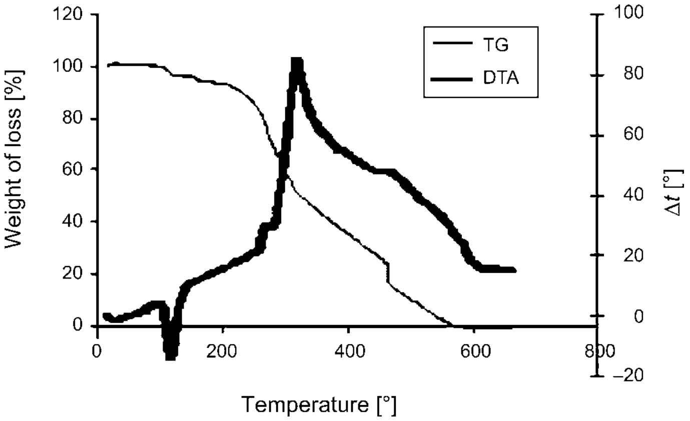

Fig. 1. *Thermal behavior of [$(DABTZ)_2$(bk)(MeOH)]*

Table 1. *Crystallographic Data for Compounds [(DABTZ)$_2$(bipy)] and [(DABTZ)$_2$(bk)(MeOH)]*

	[(DABTZ)$_2$(bipy)]	[(DABTZ)$_2$(bk)(MeOH)]
Empirical formula	$C_{16}H_{14}N_6S_2$	$C_{29}H_{44}N_8O_7S_4$
M_r	354.45	745.00
Crystal size [mm]	$0.48 \times 0.40 \times 0.27$	$0.22 \times 0.20 \times 0.17$
Temp. [K]	273(2)	298(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Z	4	2
θ Range for data collection [°]	2.28–26.30	0.95–25.30
Unit cell parameters:		
a [Å]	7.984(2)	7.4021(6)
b [Å]	21.185(6)	11.8205(9)
c [Å]	9.850(3)	21.4112(16)
α [°]	90.00	88.492(2)
β [°]	90.133(5)	87.9610(10)
γ [°]	90.00	74.7070(10)
V [Å^3]	1666.0(9)Å^3	1805.6(2)Å^3
D_x [g cm^{-3}]	1.413	1.370
Absorption coefficient [mm^{-1}]	0.330	0.318
F(000)	736	788
Index ranges	$-9 \leq h \leq 9$, $-26 \leq k \leq 20$, $-12 \leq l \leq 12$	$-8 \leq h \leq 8$, $-14 \leq k \leq 14$, $-25 \leq l \leq 25$,
Reflections collected	8100	13481
Independent reflections	3230	6526
Absorption correction	multi-scan	multi-scan
Max. and min. transmission	0.9162; 0.8577	0.9479; 0.9333
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3230/0/217	6526/0/435
Goodness-of-fit on F^2	1.080	1.184
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0534$, $wR_2 = 0.1485$	$R_1 = 0.0838$, $wR_2 = 0.1659$
R Indices (all data)	$R_1 = 0.0649$, $wR_2 = 0.1587$	$R_1 = 0.1016$, $wR_2 = 0.1758$
Largest diff. peak; hole [e Å^{-3}]	−0.477; 0.449	−0.512; 0.447

Table 2. *The H-Bonds in the Structure of [(DABTZ)$_2$(bipy)]*[a])

D–H···A	d(D–H) [Å]	d(H···A) [Å]	d(D···A) [Å]	<(DHA) [°]
N(6)–H(6B)···N(3)#3	0.86	2.30	3.067(3)	147.9
N(6)–H(6A)···N(1)#4	0.86	2.16	3.007(3)	168.7
N(4)–H(4B)···N(5)	0.86	2.31	3.072(3)	148.3

[a]) Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y$, $-z+2$; #2, $-x+1$, $-y$, $-z+1$; #3, $x+1$, y, z; #4, $-x+3/2$, $y-1/2$, $-z+3/2$.

N(2)–C(6)–C(5)–N(1) is −35.47°, whereas the dihedral angle between the two rings within both DABTZ molecules is 0.00° (*Fig. 4*). In [(DABTZ)$_2$(bk)(MeOH)], two thiazole rings of the 'DABTZ' are nearly coplanar with the dihedral

Table 3. *The H-Bonds in the Structure of [(DABTZ)$_2$(bk)(MeOH)]*[a])

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D···A) [Å]	<(DHA) [°]
N(8)–H(8D)···O(7)#5	0.86	2.03	2.885(5)	171.6
N(8)–H(8C)···N(7)#6	0.86	2.19	3.021(5)	164.0
N(7)–H(7A)···N(8)#6	0.86	2.20	3.021(5)	159.6
N(6)–H(6B)···O(4)#5	0.86	2.22	3.077(5)	171.2
N(6)–H(6A)···O(1)#5	0.86	2.61	3.205(5)	127.2
N(6)–H(6A)···O(6)#5	0.86	2.45	3.197(5)	145.4
N(5)–H(5)···O(7)#7	0.86	2.16	2.863(5)	138.5
N(4)–H(4B)···N(1)#5	0.86	2.23	3.064(5)	162.9
N(4)–H(4A)···N(3)#8	0.86	2.24	3.089(5)	171.9
N(3)–H(3)···N(4)#8	0.86	2.25	3.089(5)	166.6
N(2)–H(2B)···O(3)	0.86	2.28	3.013(5)	142.8
N(2)–H(2A)···O(5)	0.86	2.47	3.148(5)	136.9
N(1)–H(1)···N(4)#9	0.86	2.22	3.064(5)	165.8
O(7)–H(7)···N(5)#10	0.82	2.05	2.863(5)	169.1

[a]) Symmetry transformations used to generate equivalent atoms: #1, $-x+2$, $-y+1$, $-z$; #2, $-x+1$, $-y+2$, $-z$; #3, $-x$, $-y+2$, $-z+1$; #4, $-x+1$, $-y+1$, $-z+1$; #5, $x-1$, y, z; #6, $-x$, $-y+1$, $-z+1$; #7, $x-1$, $y+1$, z; #8, $-x$, $-y+2$, $-z$; #9, $x+1$, y, z; #10, $x+1$, $y-1$, z.

angle of 0.28 and $-0.79°$ (*Fig. 2*). There are π–π stacking interactions between aromatic rings belonging to two different molecules in [(DABTZ)$_2$(bipy)] and [(DABTZ)$_2$(bk)(MeOH)].

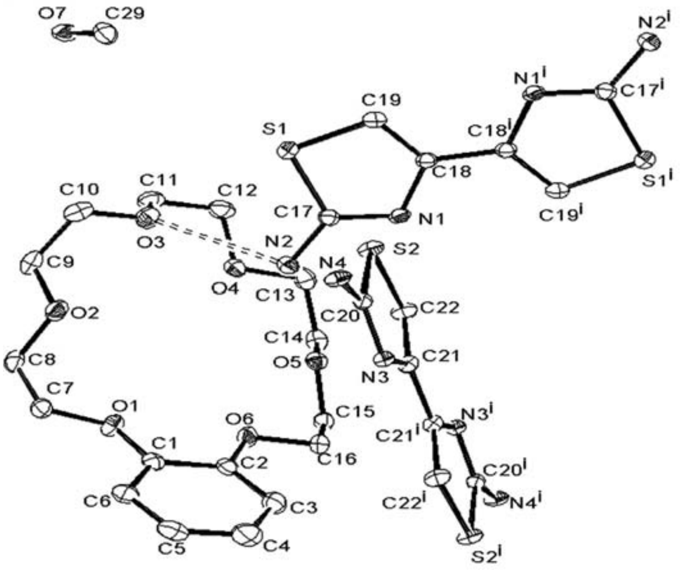

Fig. 2. *ORTEP Plot of [(DABTZ)$_2$(bk)(MeOH)] with ellipsoids of 30% probability* (DABTZ, [4,4′-Bithiazole]-2,2′-diamine; bk, benzo-18-crown-6, i: $-x$, $-y$, $-z$).

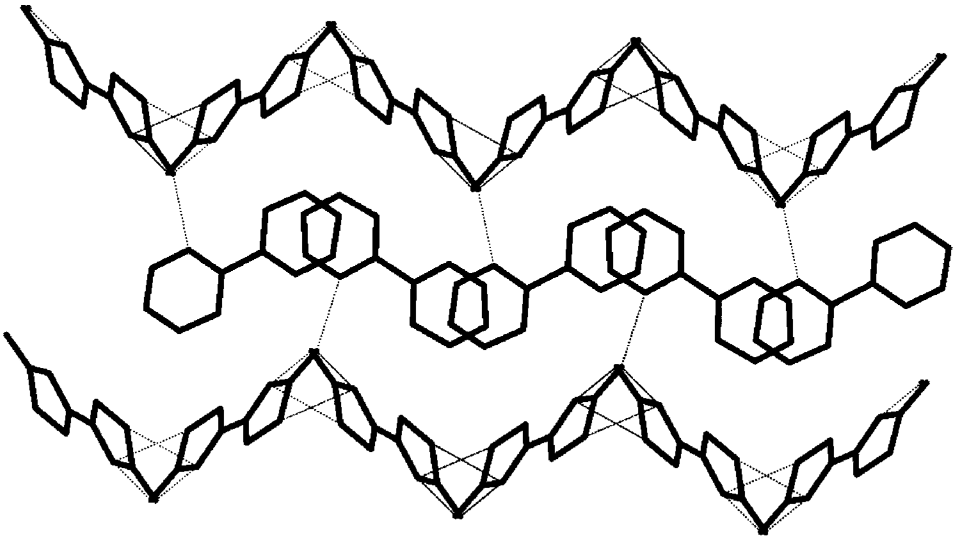

Fig. 3. *A packing diagram showing the H-bonding and π–π stacking in [(DABTZ)$_2$(bipy)].* (DABTZ, [4,4′-Bithiazole]-2,2′-diamine; bipy, 2,2′-bipyridine).

The py groups of bipy molecules in [(DABTZ)$_2$(bipy)] are almost parallel and this parallel array of the planes of the aromatic moieties indicates that these interactions are of the face-to-face 'π-stacking' type. In [(DABTZ)$_2$(bk)(MeOH)], only edge-to-face C–H(Tz)$\cdots\pi$\{TZ^{i} (i: $-x$, $-y$, $-z$)\} interactions exist between TZ groups of DABTZ molecules, and the edge-to-face distance is 3.555 Å (*Figs. 3* and *5*).

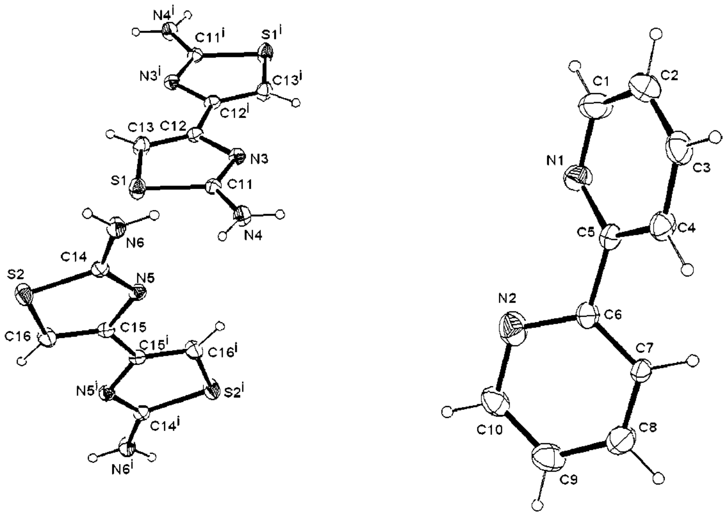

Fig. 4. *ORTEP Plot of [(DABTZ)$_2$(bipy)] with ellipsoids of 30% probability* (DABTZ, [4,4′-Bithiazole]-2,2′-diamine; bipy = 2,2′-bipyridine, i: $-x$, $-y$, $-z$).

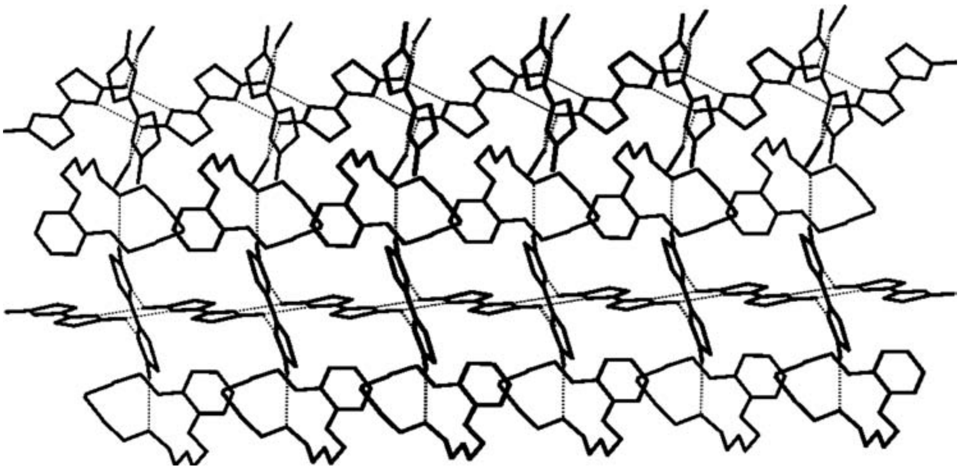

Fig. 5. *A packing diagram showing the H-bonding and π–π stacking in [(DABTZ)$_2$(bk)(MeOH)]* (DABTZ, [4,4′-Bithiazole]-2,2′-diamine; bk, benzo-18-crown-6).

Conclusions. – Attempts to isolate 1:1 adducts of co-crystals from a solution containing a mixture of [4,4′-bithiazole]-2,2′-diamine (DABTZ) with 2,2′-bipyridine (bipy) and benzo-18-crown-6 (bk) were not successful, and a new 1:2 adduct of co-crystal structures [(DABTZ)$_2$(bipy)] and [(DABTZ)$_2$(bk)(MeOH)] were isolated. Structure determination of these compounds revealed that two factors, H-bonding and π–π stacking control the packing of these two co-crystals. 2,2′-Bipyridine and benzo-18-crown-6 (bk) molecules have the best donor atom positions to form H-bonding, preventing the formation of 1:1 adducts with these molecules.

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Experimental Part

General. [4,4′-Bithiazole]-2,2′-diamine was prepared from 1,4-dibromobutane-2,3-dione and thiourea as described by *Erlenmeyer* and *Ueberwasser* [11]. M.p.: *Electrothermal 9100* apparatus. IR Spectra: *PerkinElmer 597* and *Nicolet 510P* spectrophotometers in the range of 4000–400 cm^{-1} in KBr discs; $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra: *Bruker DRX-500 AVANCE* spectrometer at 500 and 125 MHz, resp.; δ in ppm rel. to Me_4Si as internal standard, J in Hz. Elementalanalyses: *Heraeus CHN-O-Rapid* analyzer. Thermal behavior: *PL-STA 1500* apparatus.

Preparation of [([4,4′-Bithiazole]-2,2′-diamine)$_2$(2,2′-bipyridine)] ([(DABTZ)$_2$(bipy)]). The compound was prepared by dissolving [4,4′-bithiazole]-2,2′-diamine (0.198 g, 1 mmol) in MeOH (10 ml) and adding a MeOH soln. of 2,2′-bipyridine (bipy; 0.180 g, 1 mmol). The resulting soln. was stirred for 1 h at r.t. and then allowed to stand for 10 d at r.t. (*ca.* 25°). Colorless crystals of the desired product precipitated, which were filtered off and dried in air. Yield: 0.409 g (55%). M.p. 275°. IR (KBr): 545*m*, 606*m*, 816*m*, 1040*m*, 1247*m*, 1327*m*, 1523vs, 1585*s*, 1628*m*, 2850*w*, 3095*s*, 3280*s*. ^{1}H-NMR ((D$_6$)DMSO): 6.70 (*s*, 2 H); 7.15 (br. *s*, 4 H); 7.45–7.55 (*m*, 1 H); 7.95–8.15 (*m*, 1 H); 8.45 (*d*, J = 7.5, 1 H); 8.80 (*d*, J = 7.5, 1 H). ^{13}C-NMR ((D$_6$)DMSO): 102.6; 120.9; 124.5; 137.8; 146.9; 150.2; 168.7; 174.5. Anal. calc. for $C_{16}H_{20}N_{10}S_4$: C 39.94, H 4.16, N 23.95; found: C 39.30, H 4.40, N 23.60.

Preparation of [([4,4′-Bithiazole]-2,2′-diamine)$_2$(benzo-18-crown-6)(MeOH)] ([(DABTZ)$_2$(bk)(MeOH)]). The compound was prepared by dissolving [4,4′-bithiazole]-2,2′diamine (0.198 g, 1 mmol) in

MeOH (10 ml) and adding a MeOH soln. of benzo-18-crown-6 (0.312 g, 1 mmol). The resulting soln. was stirred for 1 h at r.t. and then allowed to stand for 15 d at r.t. (*ca.* 25°). Colorless crystals of the desired product precipitated, which were filtered off and dried in air. Yield: 0.190 g (50%). M.p. 257°. IR (KBr): 545*m*, 740*m*, 829*w*, 944*m*, 1034*s*, 1083*s*, 1116v*s*, 1210*s*, 1246v*s*, 1318*m*, 1440*m*, 1517v*s*, 1609*m*, 1646*m*, 3090*s*, 3215*s*, 3425*m*. ^{1}H-NMR ((D$_6$)DMSO): 3.35 (*s*, 4 H); 3.50 (*s*, 3 H); 3.70–3.85 (*m*, 8 H); 4.05–4.25 (*m*, 8 H); 6.62 (*s*, 4 H); 6.90 (*d*, $J = 7.5$, 2 H); 6.97 (*d*, $J = 7.5$, 2 H); 7.10 (br. *s*, 8 H). ^{13}C-NMR ((D$_6$)DMSO): 168.6; 147; 102.6; 113.6; 121.2; 148.7; 68.2; 68.9; 69.9; 70.5; 71.6. Anal. calc. for $C_{29}H_{44}N_8O_7S_4$: C 46.71, H 5.90, N 15.03; found: C 46.10, H 5.30, N 15.70.

Crystallography. Measurements were conducted at 273(2) K for [(DABTZ)$_2$(bipy)] and at 298(2) K for [(DABTZ)$_2$(bk)(MeOH)] with a *Bruker APEX* area-detector diffractometer. The intensity data were collected within the range of 2.28–26.30° for [(DABTZ)$_2$(bipy)] and 0.95–25.30° for [(DABTZ)$_2$(bk)(MeOH)] using graphite monochromataed MoK_α 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 [12][13].

Crystal data and structure refinements are compiled in *Table 1*. Anisotropy thermal parameters, observed and calculated structure factors, bond distances, bond angles, and torsion angles are available as supplementary material. ORTEP Diagrams and perspective views of the packing are shown in *Figs. 1–4*.

Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallography Data Centre* (*CCDC*) as deposition numbers CCDC-605745 for [(DABTZ)(bipy)] and CCDC-605744 for [(DABTZ)$_2$(bk)(MeOH)]. The data can be obtained free of charge from the *CCDC*, 12 Union Road, Cambridge CB21EZ, UK *via* fax (+44-1223 336033) or e-mail (deposit@ccdc.cam.ac.uk).

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