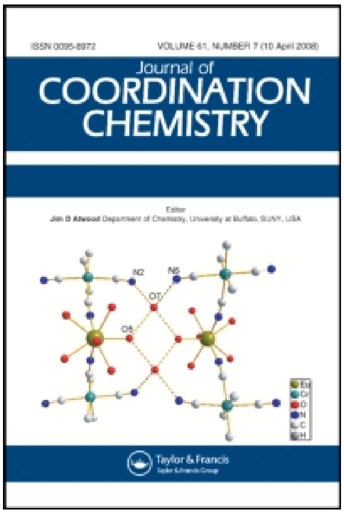

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MOLECULAR RECOGNITION OF AN ORGANIC MOLECULE BY *BIS*(TETRAFLUOROBORATE)ZINC(II). SYNTHESIS AND CRYSTAL STRUCTURE OF $\{[Zn(phen)_3](BF_4)_2\}_2 \cdot MNA \cdot (H_2O)_{1.5}$

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The 2:1 adduct $\{[Zn(phen)_3](BF_4)_2\}_2 \cdot MNA \cdot (H_2O)_{1.5}$ (1) (where phen = 1,10-phenanthroline and MNA = 2-methyl-4-nitrobenzenamine) was prepared by self-assembly and characterized by X-ray crystallography. The central zinc atom in two non-equivalent $[Zn(phen)_3]^{2+}$ cations exhibits distorted octahedral geometry with Zn–N bond distances of 2.151(6)–2.194(6) Å and 2.136(6)–2.210(6) Å, respectively. The 2-methyl-4-nitrobenzenamine molecule is connected with *bis*(tetrafluoroborate)*tris*(1,10-phenanthroline)zinc(II) through a hydrogen bond (N13-H13a···F23* 3.044 Å, *1 − *x*, 1 − *y*, − *z*). High shape specificity was observed in the recognition process.

Keywords: Zinc(II); 1,10-phenanthroline; crystal structure; molecular recognition

INTRODUCTION

Molecular recognition of guests by synthetic hosts is a rapidly developing field, and more and more self-assembled polymacrocyclic hosts have been explored recently.[1] However, few acyclic organic metal complexes were used as a host to recognize an organic guest molecule through hydrogen bonds.

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In previous work, we reported the molecular recognition ability of *bis*(perchlorato)*tris*(1,10-phenanthroline)cadmium, which could recognize *para*- and *ortho*-nitroaniline but not *meta*-nitroaniline.[2] Later, another complex, *bis*(tetrafluoroborate)*tris*(1,10-phenanthroline)cadmium(II), was also found to display shape specificity in the recognition process.[3] While 4-chloro-2-nitrobenzenamine was efficiently assembled, its isomers such as 4-chloro-3-nitrobenzenamine and 2-chloro-3-nitrobenzenamine were not recognized. As a continuation of this work, we report here the molecular recognition ability of *bis*(tetrafluoroborate)*tris*(1,10-phenanthroline)zinc(II) and the X-ray crystal structure of $\{[Zn(phen)_3](BF_4)_2\}_2 \cdot MNA \cdot (H_2O)_{1.5}$.

EXPERIMENTAL

Preparation of $\{[Zn(phen)_3](BF_4)_2\}_2 \cdot MNA \cdot (H_2O)_{1.5}$

A solution of $Zn(BF_4)_2 \cdot 6H_2O$ (1 mmol) in water (20 cm^3) was added to a solution of 1,10-phenanthroline (3 mmol) in methanol (30 cm^3) in the presence of 2-methyl-4-nitrobenzenamine (1.5 mmol). Then the solution was heated to reflux for 1 h. The resulting yellow reaction mixture was filtered and the filtrate was allowed to stand. Orange crystals of the title complex were obtained by slow evaporation of the solvent during several days (yield 45%). *Anal.*, Calc. for $C_{79}H_{59}B_4F_{16}N_{14}O_{3.5}Zn_2$(%): C, 54.58; H, 3.39; N, 11.28. Found: C, 54.3; H, 3.5; N, 11.0.

Elemental analyses were performed on a Perkin Elmer 240 instrument. IR spectra were recorded in KBr pellets in the range 4000–400 cm^{-1} in Nujol mulls using a Nicolet 170SX FTIR spectrophotometer. Thermogravimetric and differential thermal analyses were performed on a Perkin Elmer thermal analyzer under flowing N_2 with a heating rate of 10°C/min.

Crystallographic Analysis

An orange block-shaped crystal of approximate dimensions 0.36 × 0.3 × 0.2 mm was selected for X-ray analysis. The reflection data were measured on an Enraf-Nonius CAD4 diffractometer with a graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature (T = 300(2) K). The ω-2θ scan technique was employed in the range $2.32 \leq 2\theta \leq 51.92°$. Cell parameters were obtained by a least-squares fit of 25 reflections in the range $4 \leq \theta \leq 13°$. A total of 15528 reflections was collected, of which 14818 were unique ($R_{int} = 0.0221$) and 6616 with $I > 2\sigma(I)$ were used in structure

TABLE I Crystal data and data collection parameters for $\{[Zn(phen)_3](BF_4)_2\}_2 \cdot MNA \cdot (H_2O)_{1.5}$

Formula	$C_{79}H_{59}B_4F_{16}N_{14}O_{3.50}Zn_2$
Formula weight	1738.38
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	12.683(2)
b (Å)	17.499(2)
c (Å)	19.865(2)
α (°)	108.840(10)
β (°)	104.710(10)
γ (°)	103.260(10)
V (Å^3)	3795.2(8)
Z	2
T(K)	300(2)
D_{calc} (g cm^{-3})	1.521
μ (MoKα) (cm^{-1})	7.33
F(000)	1766
Collection range (°)	$3.32 < 2\theta < 51.82$
Index ranges	$-15 \le h \le 0, -20 \le k \le 21, -23 \le l \le 24$
No. of observations	15528
No. of independent reflections	14818 [R(int) = 0.0221]
Data/restraints/parameters	14818/80/1030
R ($I > 2\sigma(I)$)	0.0937
R_w ($I > 2\sigma(I)$)	0.2219
Goodness-of-fit	0.969
Largest/smallest peak in final difference map (e/Å)	1.024/−0.471

solution and refinement. The raw data were corrected for Lorentz polarization effects and absorption (Psi-scan technique).[4] Details of the crystal data and data collection are listed in Table I.

The structure was solved by the Patterson method in the SHELXS 86 program[5] and expanded using Fourier techniques to locate other non-H atoms. The structure was refined by full-matrix least-squares based on F_o^2. The cations and the organic molecule were refined anisotropically; the four BF_4^- anions were disordered and all the F atoms were refined isotropically at 0.5 site occupancy. The B–F and F···F distances were constrained in idealized tetrahedral geometry. Two water molecules, one at half occupancy, were located and refined isotropically. All hydrogen atoms on rings as well as those on CH_3 and NH_2 groups were generated geometrically and given a riding mode. The final cycle of refinement on $|F|^2$ included 1030 variable parameters and converged with $R = 0.094$, $R_w = 0.222$, where $w = 1/[\sigma^2(F_o)^2 + 0.1301P^2 + 0.0000P]$ and $P = (F_o^2 + 2F_c^2)/3$. Refinement programs used are in SHELXL-93.[6] The final atomic coordinates are listed in Table II.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $\{[Zn(phen)_3](BF_4)_2\}_2 \cdot MNA \cdot (H_2O)_{1.5}$

Atom	*x/a*	*y/b*	*z/c*	$U_{(eq)}{}^a$
Zn(1)	578(1)	6733(1)	3399(1)	49(1)
N(1)	672(6)	8077(4)	3721(3)	56(2)
N(2)	2346(5)	7409(4)	3564(3)	51(2)
C(1)	−153(8)	8396(5)	3800(5)	73(2)
C(2)	14(10)	9278(6)	4025(5)	86(3)
C(3)	1079(10)	9824(6)	4167(5)	85(3)
C(4)	1971(9)	9513(5)	4079(5)	75(3)
C(5)	3080(9)	10046(6)	4189(6)	87(3)
C(6)	3898(9)	9696(6)	4095(5)	81(3)
C(7)	3703(8)	8805(5)	3893(4)	67(2)
C(8)	4545(8)	8425(6)	3804(5)	81(3)
C(9)	4292(7)	7578(6)	3611(5)	74(2)
C(10)	3175(7)	7085(5)	3479(4)	63(2)
C(11)	2610(7)	8274(5)	3777(4)	57(2)
C(12)	1720(7)	8619(5)	3857(4)	54(2)
N(3)	814(5)	5516(4)	3320(3)	50(2)
N(4)	966(5)	6831(4)	4554(3)	51(2)
C(13)	705(6)	4852(5)	2704(4)	58(2)
C(14)	834(7)	4086(5)	2737(5)	66(2)
C(15)	1086(7)	4007(5)	3400(5)	70(2)
C(16)	1219(6)	4687(5)	4063(5)	56(2)
C(17)	1473(7)	4645(5)	4786(5)	67(2)
C(18)	1556(7)	5315(5)	5411(5)	67(2)
C(19)	1390(6)	6058(5)	5359(4)	57(2)
C(20)	1460(7)	6757(5)	5975(5)	68(2)
C(21)	1302(7)	7463(5)	5883(4)	68(2)
C(22)	1054(7)	7481(5)	5165(4)	62(2)
C(23)	1135(6)	6121(5)	4639(4)	50(2)
C(24)	1053(6)	5416(4)	3989(4)	45(2)
N(5)	−1272(5)	6274(4)	3103(3)	52(2)
N(6)	−50(5)	6304(4)	2177(3)	50(2)
C(25)	−1854(7)	6243(5)	3567(5)	68(2)
C(26)	−3061(8)	5943(6)	3305(6)	85(3)
C(27)	−3657(7)	5671(6)	2558(6)	77(3)
C(28)	−3092(6)	5696(5)	2051(5)	56(2)
C(29)	−3657(7)	5443(5)	1250(5)	73(2)
C(30)	−3074(7)	5458(5)	790(5)	68(2)
C(31)	−1812(7)	5751(5)	1080(4)	58(2)
C(32)	−1152(8)	5772(5)	618(5)	70(2)
C(33)	31(8)	6027(6)	936(5)	75(2)
C(34)	534(7)	6284(5)	1717(4)	59(2)
C(35)	−1226(6)	6036(4)	1862(4)	46(2)
C(36)	−1866(6)	6002(4)	2347(4)	49(2)
Zn(2)	3556(1)	1265(1)	2015(1)	51(1)
N(7)	3282(5)	9(4)	2002(3)	55(2)
N(8)	1901(5)	958(4)	2199(3)	54(2)
C(37)	3988(7)	−438(5)	1920(5)	68(2)
C(38)	3682(9)	−1291(6)	1837(5)	84(3)
C(39)	2622(10)	−1663(6)	1859(6)	90(3)
C(40)	1872(8)	−1211(5)	1956(5)	68(2)
C(41)	768(10)	−1550(6)	2002(6)	90(3)
C(42)	132(9)	−1060(7)	2174(5)	83(3)
C(43)	505(7)	−182(6)	2269(4)	64(2)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	$U_{(eq)}{}^{a}$
C(44)	−96(7)	376(7)	2488(5)	74(2)
C(45)	293(8)	1192(7)	2536(5)	83(3)
C(46)	1268(7)	1454(6)	2364(5)	68(2)
C(47)	1533(6)	158(5)	2164(4)	50(2)
C(48)	2237(7)	−361(5)	2030(4)	56(2)
N(9)	3516(5)	2535(4)	2195(4)	55(2)
N(10)	4592(5)	1975(4)	3196(3)	53(2)
C(49)	5088(7)	1682(6)	3678(5)	66(2)
C(50)	5786(8)	2230(8)	4443(5)	84(3)
C(51)	5901(8)	3066(8)	4682(6)	90(3)
C(52)	5403(7)	3397(6)	4203(5)	72(3)
C(53)	5507(10)	4277(7)	4409(7)	100(4)
C(54)	4954(11)	4551(6)	3902(8)	103(4)
C(55)	4253(8)	3983(5)	3149(6)	73(3)
C(56)	3630(11)	4238(7)	2619(8)	98(4)
C(57)	3000(10)	3657(7)	1928(8)	95(3)
C(58)	2953(7)	2813(6)	1719(5)	72(2)
C(59)	4155(7)	3113(5)	2920(5)	58(2)
C(60)	4731(6)	2813(5)	3438(4)	56(2)
N(11)	2922(5)	842(4)	800(3)	59(2)
N(12)	5147(5)	1375(4)	1734(3)	52(2)
C(61)	1833(7)	562(6)	333(5)	80(3)
C(62)	1518(8)	342(7)	−445(5)	96(3)
C(63)	2336(8)	418(6)	−744(5)	82(3)
C(64)	3527(7)	725(5)	−275(4)	57(2)
C(65)	4450(8)	827(5)	−560(4)	65(2)
C(66)	5549(7)	1094(5)	−107(5)	64(2)
C(67)	5837(6)	1290(4)	689(4)	49(2)
C(68)	6981(7)	1566(5)	1203(5)	65(2)
C(69)	7171(7)	1726(5)	1952(5)	70(2)
C(70)	6233(7)	1618(5)	2184(4)	61(2)
C(71)	4953(6)	1205(4)	996(4)	48(2)
C(72)	3775(6)	919(4)	495(4)	48(2)
O(1)	6454(6)	3674(5)	2635(4)	106(2)
O(2)	8152(6)	4022(5)	2598(4)	106(2)
N(13)	5240(8)	2950(5)	−821(5)	102(3)
N(14)	7099(7)	3759(5)	2281(5)	76(2)
C(73)	5717(11)	3151(6)	−54(6)	85(3)
C(74)	6901(9)	3364(6)	310(6)	83(3)
C(75)	7353(8)	3565(5)	1061(6)	74(2)
C(76)	6615(8)	3542(5)	1481(6)	68(2)
C(77)	5445(8)	3322(5)	1132(6)	68(2)
C(78)	4967(8)	3118(5)	364(6)	75(3)
C(79)	3645(11)	2892(7)	−32(6)	119(4)
B(1)	2648(7)	2586(5)	4657(5)	117(5)
F(11)	2564(12)	2969(8)	4134(6)	147(5)
F(12)	1724(9)	2488(8)	4859(8)	137(5)
F(13)	3661(8)	3102(7)	5267(5)	113(4)
F(14)	2775(10)	1821(5)	4303(6)	105(4)
F(11′)	3429(10)	3373(6)	5002(8)	153(6)
F(12′)	1554(8)	2650(9)	4466(8)	148(6)
F(13′)	2677(16)	2197(10)	5177(8)	229(9)
F(14′)	2772(12)	2046(8)	4049(7)	145(6)

TABLE II (*Continued*)

Atom	x/a	y/b	z/c	$U_{(eq)}$[a]
B(2)	3174(6)	5721(4)	1584(4)	84(3)
F(21)	3781(8)	5872(6)	2314(4)	87(3)
F(22)	3616(8)	5330(6)	1087(5)	83(4)
F(23)	3058(8)	6457(5)	1540(5)	73(3)
F(24)	2054(7)	5155(6)	1432(6)	103(4)
F(21′)	4285(7)	6316(7)	2069(6)	140(5)
F(22′)	3383(8)	5036(5)	1111(5)	73(3)
F(23′)	2670(8)	6103(6)	1158(6)	92(3)
F(24′)	2609(9)	5491(6)	2000(6)	98(3)
B(3)	− 347(8)	2032(7)	433(5)	170(8)
F(31)	− 1475(9)	1897(11)	45(8)	180(8)
F(32)	349(14)	2692(11)	351(10)	212(8)
F(33)	− 217(12)	2236(10)	1175(5)	134(5)
F(34)	− 69(15)	1320(9)	139(9)	193(7)
F(31′)	− 1437(8)	1460(9)	− 35(7)	129(5)
F(32′)	− 402(19)	2837(8)	708(13)	310(14)
F(33′)	14(15)	1791(13)	1021(9)	216(10)
F(34′)	419(12)	2023(16)	71(10)	234(9)
B(4)	2831(8)	9949(6)	6668(6)	160(7)
F(41)	1743(9)	9619(10)	6122(8)	161(7)
F(42)	3523(13)	9650(12)	6272(10)	210(10)
F(43)	3235(15)	10812(6)	6951(11)	224(9)
F(44)	2859(14)	9647(12)	7208(8)	187(7)
F(41′)	1684(8)	9454(8)	6378(8)	132(6)
F(42′)	3502(13)	9468(10)	6576(11)	199(9)
F(43′)	2980(13)	10536(9)	6357(10)	165(6)
F(44′)	3102(14)	10404(12)	7444(6)	208(8)
O(1W)	2901(12)	12183(9)	7828(8)	228(5)
O(2W)	2855(18)	11962(13)	6287(12)	169(7)

[a] $U_{(eq)}$ is defined as one third of the trace of the orthogonalised U_{ij} tensor.

RESULTS AND DISCUSSION

Preparation

Crystallization of *bis*(tetrafluoroborate)*tris*(1,10-phenanthroline)zinc(II) in the presence of suitable guest molecule, *i.e.*, 2-methyl-4-nitrobenzenamine gives a co-crystal 2 : 1 adduct $\{[Zn(phen)_3](BF_4)_2\}_2{\cdot}MNA{\cdot}(H_2O)_{1.5}$. This is very similar to the crystallization of *bis*(perchlorato)*tris*(1,10-phenanthroline)-cadmium(II) in the presence of *para*-nitroaniline to obtain $[Cd(phen)_3](ClO_4)_2{\cdot}2PNA$[2] and co-crystallization of *bis*(tetrafluoroborate)*tris*(1,10-phenanthroline)cadmium(II) with 4-chloro-2-nitrobenzenamine to prepare $[Cd(phen)_3](BF_4)_2{\cdot}2CNA$.[3] The former reaction yields a co-crystal 2 : 1 adduct product $\{[Zn(phen)_3](BF_4)_2\}_2{\cdot}MNA{\cdot}(H_2O)_{1.5}$, whereas the latter reactions both form 1 : 2 products $[Cd(phen)_3](ClO_4)_2{\cdot}2PNA$[2] and $[Cd(phen)_3]$-$(BF_4)_2{\cdot}2CNA$,[3] respectively. This stoichiometric difference may be attributed to the smaller radius of the zinc(II) ion with respect to cadmium(II) ion.

High shape selectivity in the recognition process was observed. While 2-methyl-4-nitrobenzenamine was efficiently assembled, its isomers such as 4-methyl-3-nitrobenzenamine and 4-methyl-2-nitrobenzenamine were not recognized. In addition, *para-*, *meta-* and *ortho*-nitroaniline were not recognized by *bis*(tetrafluoroborate)*tris*(1,10-phenanthroline)zinc(II). On the other hand, although the guest molecule 2-methyl-4-nitrobenzenamine was efficiently recognized by *bis*(tetrafluoroborate)*tris*(1,10-phenanthroline)-zinc(II), it failed to be recognized by *bis*(perchlorato)*tris*(1,10-phenanthroline)cadmium(II) and *bis*(tetrafluoroborate)*tris*(1,10-phenanthroline) cadmium(II). Similar shape selectivity was also observed in the recognition of *para*-nitroaniline by $[Cd(phen)_3](ClO_4)_2$ and the recognition of 4-chloro-2-nitrobenzenamine by $[Cd(phen)_3](BF_4)_2$. This discrimination of isomers in the recognition process could be applied to separating of one kind of organic guest molecule from its isomeric mixture.[3,7] For example, in the crystallization of *bis*(tetrafluoroborate)*tris*(1,10-phenanthroline)zinc(II) in the presence of a mixture of 2-methyl-4-nitrobenzenamine, 4-methyl-3-nitrobenzenamine and 4-methyl-2-nitrobenzenamine (1 : 1 : 1), only the co-crystal **1** was obtained, from which 2-methyl-4-nitrobenzenamine was recovered by acid decomposition followed by recrystallization.

Description of the Structure

As shown in Figure 1, the asymmetric unit of the structure consists of two crystallographically independent $[Zn(phen)_3]^{2+}$ cations, four BF_4^- anions, one and one half water molecules and one 2-methyl-4-nitrobenzenamine molecule. The packing arrangement of **1** in the unit cell is shown in Figure 2. Selected bond distances and angles for **1** are listed in Table III. Two crystallographically independent cations form a "diad" in which each zinc atom is coordinated to six N atoms from three phenanthroline to form a slightly distorted octahedral geometry. The local coordination environment is very similar to that in $[Cd(phen)_3](ClO_4)_2 \cdot 2PNA$[2] and $[Cd(phen)_3](BF_4)_2 \cdot 2CNA$.[3] The Zn–N bond lengths are in the expected range[8] Zn(1)–N distances range from 2.151(6) to 2.194(6) Å, whereas Zn(2)–N distances fall in the range 2.136(6)–2.210(6) Å, suggesting Zn(2) has a more distorted octahedral geometry with respect to Zn(1). This is also confirmed by the fact that the range of *trans-* bond angles N–Zn(2)–N (162.2(2)–171.8(2)°) is larger than that of N–Zn(1)–N (165.6(2)–167.0(2)°).

The benzene rings of 2-methyl-4-nitrobenzenamine molecules run in the (0 3 1) direction, each of them separates two $[Zn(phen)_3]^{2+}$ anions. This

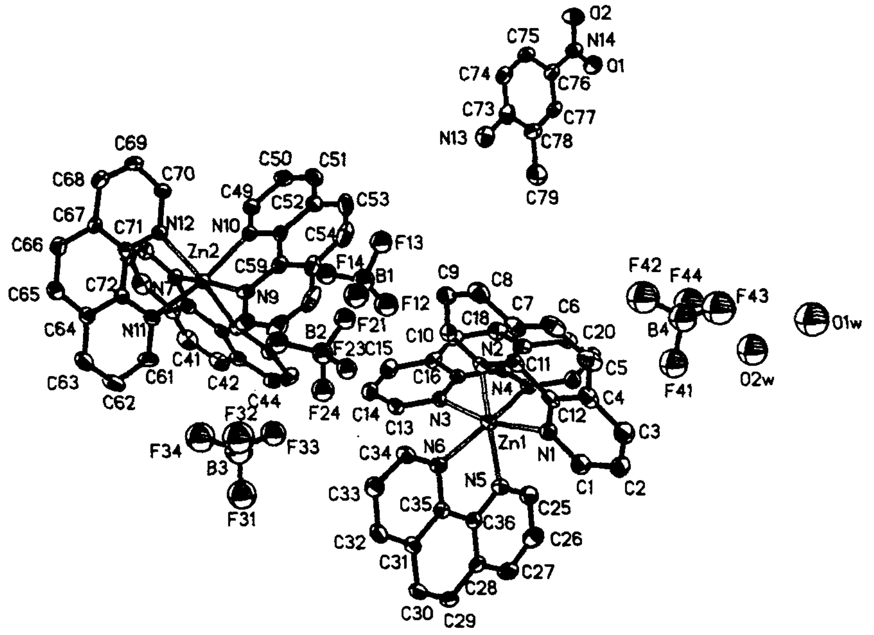

FIGURE 1 Structure and numbering scheme for $\{[Zn(phen)_3](BF_4)_2\}_2 \cdot MNA \cdot (H_2O)_{1.5}$.

arrangement is quite different from that in $[Cd(phen)_3](ClO_4)_2 \cdot 2PNA$[2] and $[Cd(phen)_3](BF_4)_2 \cdot 2CNA$.[3] In $[Cd(phen)_3](ClO_4)_2 \cdot 2PNA$, two *para*-nitrobenzenamine molecules are situated on two opposite sides of $[Cd(phen)_3]^{2+}$ and have no connection with each other,[2] whereas in $[Cd(phen)_3](BF_4)_2 \cdot 2CNA$ the two 4-chloro-2-nitrobenzenamine molecules are connected to each other by intermolecular hydrogen bonds and packed with the planes of the guest molecules parallel to the phenanthroline ligands. The main cause should be attributed to both the stoichiometric differences and guest molecule effects.

The 2-methyl-4-nitrobenzenamine molecule connects with two $[Znphen_3](BF_4)_2$ through the hydrogen bond ($N13-H13^a \cdots F23$ 3.044 Å; symmetry code: $^a1-x,\ 1-y,\ -z$). Similar trends were also observed in $[Cd(phen)_3](ClO_4)_2 \cdot 2PNA$[2] and $[Cd(phen)_3](BF_4)_2 \cdot 2CNA$.[3] In addition, this packing structure is also stabilized by hydrogen bonds between 2-methyl-4-nitrobenzenamine and water ($N13-H13^b \cdots O1w$ 3.099; $^bx,\ -1+y,\ -1+z$), BF_4^- and water ($O1w \cdots F43$ 2.667; $O2w \cdots F43$ 2.804) as well as both water molecules ($O1w-H1w \cdots O2w$ 2.94(2)), whereas in $[Cd(phen)_3](ClO_4)_2 \cdot 2PNA$[2] and $[Cd(phen)_3](BF_4)_2 \cdot 2CNA$[3] no such hydrogen bonds exist.

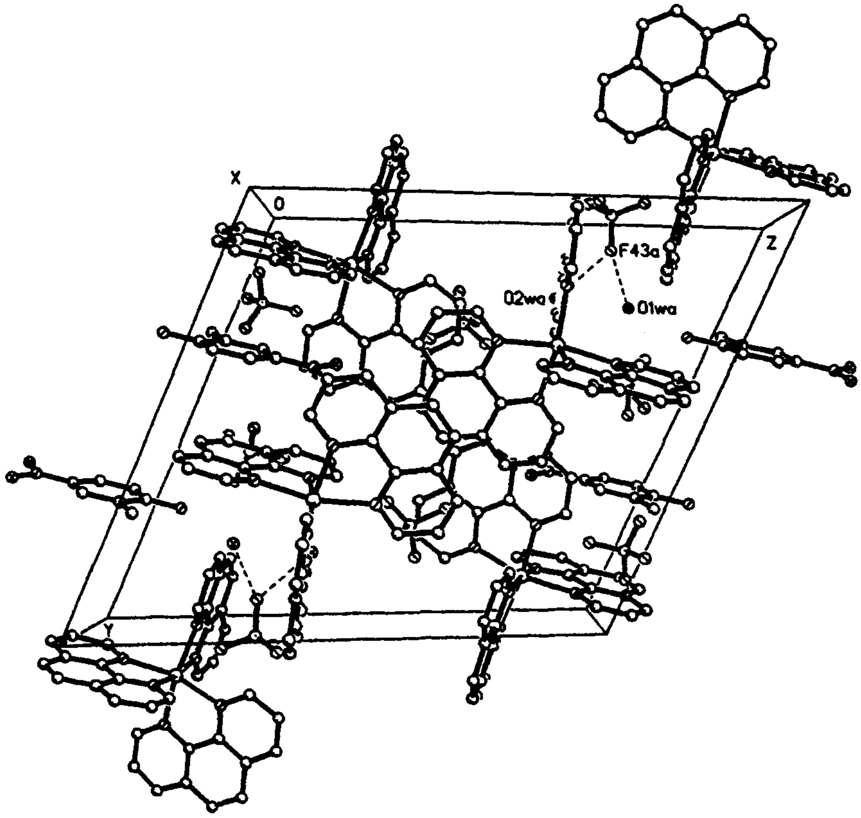

FIGURE 2 Unit cell molecular packing of $\{[Zn(phen)_3](BF_4)_2\}_2\cdot MNA\cdot(H_2O)_{1.5}$ viewed down the *a* axis.

IR Spectra and Thermogravimetric Analysis

In the IR spectrum, there are at least seven bands in the 3000–3680 cm^{-1} region. Two sharp bands at 3480 cm^{-1} and 3389 cm^{-1} may be assigned to the NH_2 stretching vibrations of 2-methyl-4-nitrobenzenamine, which are comparable with those in $[Cd(phen)_3](ClO_4)_2\cdot 2PNA$ (3450 and 3362 cm^{-1})[2] and $[Cd(phen)_3](BF_4)_2\cdot 2CNA$ (3490 and 3375 cm^{-1});[3] four relatively broad bands around 3649, 3547, 3497 and 3464 cm^{-1} must be attributed to the H–O–H stretching vibrations of the water molecules.[9] The sharp band at 3065 cm^{-1} may be assigned to the C–H stretching vibration of the benzene or phenanthroline ring. The very strong band at 1063 cm^{-1} is attributed to tetrafluoroborate. Such a result indicates that tetrafluoroborate is not coordinated to zinc(II).[10]

TABLE III Selected bond distances (Å) and angles (°) for $\{[Zn(phen)_3](BF_4)_2\}_2 \cdot MNA \cdot (H_2O)_{1.5}$

Zn(1)–N(5)	2.151(6)	Zn(2)–N(7)	2.136(6)
Zn(1)–N(6)	2.158(6)	Zn(2)–N(10)	2.138(6)
Zn(1)–N(4)	2.160(6)	Zn(2)–N(11)	2.146(6)
Zn(1)–N(2)	2.167(6)	Zn(2)–N(9)	2.147(6)
Zn(1)–N(3)	2.179(6)	Zn(2)–N(8)	2.197(6)
Zn(1)–N(1)	2.194(6)	Zn(2)–N(12)	2.210(6)
N(5)–Zn(1)–N(6)	77.4(2)	N(7)–Zn(2)–N(10)	97.5(2)
N(5)–Zn(1)–N(4)	94.8(2)	N(7)–Zn(2)–N(11)	95.4(2)
N(6)–Zn(1)–N(4)	165.6(2)	N(10)–Zn(2)–N(11)	162.2(2)
N(5)–Zn(1)–N(2)	165.6(2)	N(7)–Zn(2)–N(9)	164.5(2)
N(6)–Zn(1)–N(2)	95.0(2)	N(10)–Zn(2)–N(9)	78.0(2)
N(4)–Zn(1)–N(2)	95.0(2)	N(11)–Zn(2)–N(9)	92.5(2)
N(5)–Zn(1)–N(3)	96.0(2)	N(7)–Zn(2)–N(8)	76.8(2)
N(6)–Zn(1)–N(3)	91.8(2)	N(10)–Zn(2)–N(8)	95.2(2)
N(4)–Zn(1)–N(3)	76.7(2)	N(11)–Zn(2)–N(8)	99.7(2)
N(2)–Zn(1)–N(3)	96.5(2)	N(9)–Zn(2)–N(8)	88.8(2)
N(5)–Zn(1)–N(1)	93.0(2)	N(7)–Zn(2)–N(12)	96.1(2)
N(6)–Zn(1)–N(1)	99.3(2)	N(10)–Zn(2)–N(12)	89.8(2)
N(4)–Zn(1)–N(1)	93.2(2)	N(11)–Zn(2)–N(12)	76.6(2)
N(2)–Zn(1)–N(1)	76.0(2)	N(9)–Zn(2)–N(12)	98.6(2)
N(3)–Zn(1)–N(1)	167.0(2)	N(8)–Zn(2)–N(12)	171.8(2)
Relevant H bond distances (Å) and angles (°)			
N13–H13a···F23	3.044	N13–H13b···O1w	3.099
O1w–H1w···O2w	2.94(2)	O1w···F43	2.667
O2w···F43	2.804		

Symmetry codes: (a) $1-x, 1-y, -z$; (b) $x, -1+y, -1+z$.

Thermogravimetric analysis (TGA) of **1** reveals that the first decomposition event takes place from 30°C to 185°C (endothermic). On the base of weight change, this process corresponds to the loss of water (found: 1.7%; calcd: 1.55%). The second weight loss occurs at 258°C, and corresponds to the loss of 2-methyl-4-nitrobenzenamine with an endothermic peak (found: 8.2%; calcd: 8.69%). This temperature for loss of guest molecule is comparable with that of $[Cd(phen)_3](ClO_4)_2 \cdot 2PNA$ (247°C)[2] but higher than that of $[Cd(phen)_3](BF_4)_2 \cdot 2CNA$ (204°C).[3] Finally, at 341°C, $[Zn(phen)_3](BF_4)_2$ begins to decompose.

Supplementary Material

H atom positions, thermal parameters and lists of observed and calculated structure factors are available from the authors on request.

Acknowledgments

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