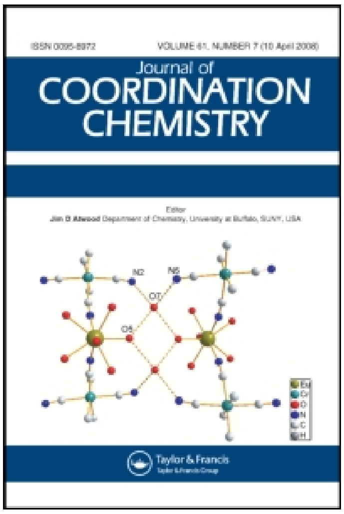

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MOLECULAR RECOGNITION OF AN ORGANIC MOLECULE THROUGH FORMING A CO-CRYSTAL COMPLEX Synthesis and Crystal Structure of [Cdphen$_3$](BF$_4$)$_2$-2CNA

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MOLECULAR RECOGNITION OF AN ORGANIC MOLECULE THROUGH FORMING A CO-CRYSTAL COMPLEX

Synthesis and Crystal Structure of $[Cdphen_3](BF_4)_2 \cdot 2CNA$

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The co-crystal 1:2 adduct $[Cdphen_3](BF_4)_2 \cdot 2CNA$ (**1**) (phen = phenanthroline-N^1,N^{10} and CNA = 4-chloro-2-nitro-benzenamine) has been prepared by crystallization of *bis*(tetrafluoroborate)*tris*(phenanthroline)cadmium(II), $[Cdphen_3](BF_4)_2$, in the presence of 4-chloro-2-nitrobenzenamine. Single crystal X-ray analysis revealed that the cadmium(II) ion exhibits a distorted octahedral geometry with Cd-N bond distances of 2.337(3)-2.374(3)Å. The organic guest molecules are packed with the plane of the molecules parallel to the phenanthroline ligands. Both intra- and intermolecular hydrogen bonding is important in the complex.

Keywords: cadmium(II), phenathroline-N^1, molecular recognition, crystal structure

INTRODUCTION

Recognition of molecular shapes and functions is currently one of the most rapidly developing areas in organic and inorganic chemistry [1]. To the best of our knowledge, strong (O-H···O and N-H···O hydrogen bonds), weak (Van der Waals, $\pi \cdots \pi$ stacking) and potentially weak (C-H···Y hydrogen bonds, Y=O, N) intermolecular interactions generally play an important role in the process of

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molecular recognition and self-assembly of molecules [2]. In previous work, we reported a novel co-crystal complex *bis*(perchlorato)*tris*(phenanthroline-N^1,N^{10})cadmium*bis(para*-nitroaniline), $[Cdphen_3](ClO_4)_2 \cdot 2PNA$, with hydrogen bonds between an organic, nonlinear optical (NLO) molecule and a metal complex [3]. It was surprisingly found that the perchlorate anion in *bis*(perchlorato)*tris*(phenantroline-N^1,N^{10}) cadmium could display shape specificity in the recognition process to some degree. Following our interest in the chemistry of recognition of molecular shape, we decided to extend our research on molecular recognition using a new anion. This paper reports the molecular recognition of 4-chloro-2-nitro-benzenamine by tetrafluoroborate in *bis*(tetrafluoroborate)*tris*(phenathroline-N^1,N^{10}) cadmium(II) and the X-ray crystal structure of the co-crystal 1:2 adduct $[Cdphen_3](BF_4)_2 \cdot 2CNA$ (phen = phenathroline-N^1,N^{10}; CNA = 4-chloro-2-nitrobenzenamine).

EXPERIMENTAL

Synthesis of $[Cdphen_3](BF_4)_2 \cdot 2CNA$

All chemicals were procured commercially and used without subsequent purification. The complex $[Cdphen_3](BF_4)_2 \cdot 2CNA$ was prepared by refluxing an ethanol solution of phenathroline-N^1,N^{10} (3 mmol), $Cd(BF_4)_2 \cdot 6H_2O$ (1 mmol) and 4-chloro-2-nitrobenzenamine (2 mmol) for 1h. After the solution was cooled to room temperature, the fitrate was left to evaporate for several days to give orange crystals of the title complex. Crystals for elemental analyses were dried *in vacuo*. Yield 67.8%. *Anal.*, Calc. for $C_{48}H_{34}B_2Cl_2F_8N_{10}O_4Cd$ (%): C, 49.2; H, 2.9; N, 12.0. Found: C, 49.1; H, 2.9; N, 11.9.

Elemental analyses were performed on a Perkin Elmer 240 instrument. IR spectra were recorded in KBr pellets in the range 4000-400 cm^{-1} and for 500-100 cm^{-1} in Nujol mulls using a Nicolet 170SX FTIR spectrophotometer. Thermogravimetric and difference 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-like crystal with dimensions 0.57 × 0.57 × 0.57 mm was used for data collection at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated MoKα radiation (λ = 0.71069 Å) using the ω-2Θ scan technique. Details of the crystal data and data collection are listed in Table I. Cell parameters were obtained by a least-squares fit of 25 reflections in the range $4.5 < \Theta < 11°$, A total of 4313 independent reflections were measured

TABLE I Crystal data and data collection parameters for [Cdphen$_3$] (BF$_4$)$_2$·2CNA.

Formula	$C_{48}H_{34}B_2Cl_2F_8N_{10}O_4Cd$
Formula weight	1171.77
Crystal system	Orthorhombic
Space group	*Pbcn*
a(Å)	13.861(6)
b(Å)	15.898(2)
c(Å)	22.285(8)
Z	4
T (K)	300(2)
D_{calc} (gcm^{-3})	1.585
F(000)	2352
μ(MoKα) (cm^{-1})	6.40
Collection range (°)	$3.66 < 2\theta < 49.94°$
Index ranges	$0 \leq h \leq 16, 0 \leq k \leq 18, 0 \leq l \leq 26$
No. of observations	4313
No. of independent reflections	4313 [$R(int) = 0.0000$]
R ($I > 2\sigma(I)$)	0.045
R_w ($I > 2\sigma(I)$)	0.099
R (all date)	0.082
R_w (all data)	0.111
Goodness-of-fit	0.978
Smallest/largest peak in final difference map (e/Å)	−0.514/0.386

in the range $3.66° \leq 2\Theta \leq 49.94°$, of which 2664 were observed with $I > 2\sigma(I)$ and used in structure solution and refinement. The raw data were corrected for Lorentz polarization effects and absorption (Psi-scan technique) [4].

The structure was solved by using the direct method in the SHELXS86 program [5]. The structure was refined by full-matrix least-squares on F_o^2 (data/restraints/parameters: 4313/0/339), converging to $R = 0.046$, $R_w = 0.099$ ($I > 2\sigma(I)$ observed data); $R = 0.082$, $R_w = 0.111$ (all data). H atoms were generated geometrically and allowed to ride on their respective parent atoms. Refinement programs used are in SHELXL-93 [6]. The final atomic coordinates are listed in Table II.

RESULTS AND DISCUSSION

Preparation

When suitable guest molecules such as 4-chloro-2-nitrobenzenamine are present, crystallization of *bis*(tetrafluoroborate)*tris*(phenanthroline)cadmium(II) yield a co-crystal 1:2 adduct [Cdphen$_3$](BF$_4$)$_2$·2CNA, similar to the reaction of *para*-nitroaniline and [Cdphen$_3$](ClO$_4$)$_2$ [3]. It should be noted that the tetrafluoroborate anion in [Cdphen$_3$](BF$_4$)$_2$·2CNA exhibits shape selectivity in the

TABLE II Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for [Cdphen$_3$] $(BF_4)_2$·2CNA.

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*[†]
Cd	0	6085(1)	2500	49(1)
Cl	942(1)	4514(2)	487(1)	152(1)
F(1)	1051(3)	804(2)	3363(1)	147(2)
F(2)	2086(2)	1267(2)	4058(2)	148(2)
F(3)	537(2)	1276(2)	4229(2)	118(1)
F(4)	1310(2)	51(2)	4178(1)	104(1)
O(1)	2392(3)	3231(3)	2405(2)	134(2)
O(2)	3916(3)	3389(3)	2421(2)	105(1)
N(1)	−181(2)	6857(2)	1615(1)	49(1)
N(2)	1527(2)	6248(2)	2067(1)	51(1)
N(3)	535(2)	4871(2)	3024(1)	56(1)
N(4)	3134(4)	3501(3)	2184(2)	81(1)
N(5)	4801(3)	4134(3)	1533(2)	82(1)
B	1268(4)	851(4)	3956(3)	72(2)
C(1)	−990(3)	7163(3)	1397(2)	62(1)
C(2)	−1062(3)	7535(3)	829(2)	76(1)
C(3)	−258(3)	7598(3)	487(2)	76(1)
C(4)	618(3)	7291(3)	705(2)	59(1)
C(5)	1497(4)	7363(3)	376(2)	77(1)
C(6)	2332(4)	7085(3)	604(2)	77(1)
C(7)	2378(3)	6709(3)	1182(2)	60(1)
C(8)	3244(3)	6414(3)	1439(2)	71(1)
C(9)	3234(3)	6055(3)	1990(2)	69(1)
C(10)	2354(3)	5978(3)	2289(2)	62(1)
C(11)	1531(3)	6613(2)	1517(2)	50(1)
C(12)	631(3)	6921(2)	1277(2)	48(1)
C(13)	1040(3)	4859(3)	3525(2)	69(1)
C(14)	1331(4)	4126(3)	3809(2)	81(2)
C(15)	1061(4)	3375(3)	3566(2)	78(1)
C(16)	525(3)	3354(3)	3040(2)	61(1)
C(17)	250(3)	2592(3)	2757(2)	78(2)
C(18)	271(3)	4128(3)	2777(2)	53(1)
C(19)	3066(3)	3904(3)	1608(2)	64(1)
C(20)	2154(3)	4009(3)	1350(2)	78(1)
C(21)	2065(4)	4382(4)	810(2)	84(2)
C(22)	2883(4)	4658(3)	500(2)	85(2)
C(23)	3766(4)	4564(3)	744(2)	76(1)
C(24)	3909(3)	4196(3)	1314(2)	64(1)

[†] *U(eq)* is defined as one third of the trace of the orthogonalized U_{ij} tensor.

recognition process, to some extent. While 4-chloro-2-nitrobenzenamine was efficiently assembled, its isomers 4-chloro-3-nitrobenzenamine, 3-chloro-5-nitrobenzenamine and 2-chloro-4-nitrobenzenamine were not recognized. A similar trend was observed in the recognition process by $[Cdphen_3](ClO_4)_2$; the perchlorato anion in the latter only recognized *para-* and *ortho-*nitroaniline,

TABLE III Selected bond distances (Å) and angles (°) for [Cdphen$_3$](BF$_4$)$_2$·2CNA.[‡]

Cd-N(1)	2.337(3)	Cd-N(2)	2.341(3)
Cd-N(3)	2.374(3)	Cl-C(21)	1.728(5)
N(4)-C(19)	1.436(6)	N(5)-C(24)	1.333(5)
O(1)-N(4)	1.218(5)	O(2)-N(4)	1.220(5)
N(1)$^{\#1}$-Cd-N(1)	116.6(2)	N(1)-Cd-N(2)$^{\#1}$	101.1(1)
N(1)-Cd-N(2)	72.02(11)	N(2)2$^{\#1}$-Cd-N(2)	167.3(2)
N(1)-Cd-N(3)	151.1(1)	N(1)-Cd-N(3)$^{\#1}$	88.8(1)
N(2)-Cd-N(3)$^{\#1}$	99.8(1)	N(2)-Cd-N(3)	90.6(1)
N(3)$^{\#1}$-Cd-N(3)	71.2(2)	O(2)-N(4)-O(1)	121.4(5)
O(2)-N(4)-C(19)	120.8(4)	O(1)-N(4)-C(19)	117.7(5)
Relevant H bond distances (Å)			
N(5)-H(5a)···F(4)$^{\#2}$	3.002	N(5)-H(5b)···O(2)	2.613
N(5)-H(5b)···O(2)$^{\#3}$	3.162		

[‡] Symmetry code: $^{\#1}1 - x, -y, 0.5 - z$; $^{\#2}0.5 + x, 0.5 + y, 0.5 - z$; $^{\#3}1 - x, y, 0.5 - z$.

while the *meta*-isomer was not efficiently assembled. This shape selectivity recognition of [Cdphen$_3$](BF$_4$)$_2$ may be due to formation of intermolecular hydrogen bonding as shown in the packing diagram of [Cdphen$_3$](BF$_4$)$_2$·2CNA. Former researchers indicated that discrimination of the isomers in the recognition process could be applied to separating of one kind of organic guest molecule from its isomeric mixture [7]. Hence, from a mixture of 4-chloro-3-nitrobenzenamine, 3-chloro-5-nitrobenzenamine, 2-chloro-4-nitrobenzenamine and 4-chloro-2-nitrobenzenamine (1:1:1:1), only the co-crystal **1** formed, from which 4-chloro-2-nitrobenzenamine was recovered with 99% purity by acidic decomposition of the co-crystal followed by recrystallization.

Description of the Structure

Selected bond distances and angles for [Cdphen$_3$](BF$_4$)$_2$·2CNA are listed in Table III. Figures 1 and 2 show part of the molecular configuration and the packing arrangement of [Cdphen$_3$](BF$_4$)$_2$·2CNA in the unit cell, respectively. The compound is formed from discrete [Cdphen$_3$]$^{2+}$ cations, BF$_4^-$ anions and 4-chloro-2-nitrobenzenamine molecules. The coordination geometry of the cadmium(II) atom closely resembles that in [Cdphen$_3$](ClO$_4$)$_2$·2PNA [3]. A distorted octahedral geometry is formed in which the Cd atom, coordinated to six N atoms from three phenanthroline molecules, lies on a 2-fold axis. The Cd-N bond lengths (2.337(3)-2.374(3) Å) are in accordance with those of [Cdphen$_3$](ClO$_4$)$_2$·2PNA (2.332(3)-2.366(4)Å) [3] and *bis[N*-(2-pyridinylmethyl)-2-pyridinemethanamine-*N*^{1}, *N*^{2}, *N*$^{2\prime}$]cadmium(II) diperchlorate (2.338(3)-2.370(4)Å)

[8], but are slightly shorter than those in *hexakis*(2-methylimidazole)cadmium(II) tetrafluoroborate (2.413(3)Å) [9].

N-Cd-N bond angles formed at Cd atom with two N atoms from the same phenanthroline ligands (71.9(2)-72.0(1)°) are comparable to those in [Cdphen$_3$](ClO$_4$)$_2$·2PNA (71.7(1)°) [3], while the N-Cd-N bond angles formed with two N atoms from different phenanthroline ligands (88.8(1)-167.3(2)°) are significantly different from those in [Cdphen$_3$](ClO$_4$)$_2$·2PNA (95.5(1)-159.6(2)°). This may be due to the arrangement of guest molecules in the two kinds of complexes being quite different. In [Cdphen$_3$](ClO$_4$)$_2$·2PNA, the two *para*-nitroaniline molecules have no connection with each other and are situated on the outside of the two discrete ClO_4^- anions, whereas in [Cdphen$_3$](BF$_4$)$_2$·2CNA the two 4-chloro-2-nitrobenzenamine molecules are connected to each other by intermolecular hydrogen bonds (N(5)-H(5b)···O(2)$^{\#3}$ 3.162Å, symmetry code: 1-*x*, *y*, 0.5-*z*), and packed with the plane of the molecules parallel to the phenanthroline ligands. In addition, another intermolecular hydrogen bond (N(5)-H(5a)···F(4)$^{\#2}$

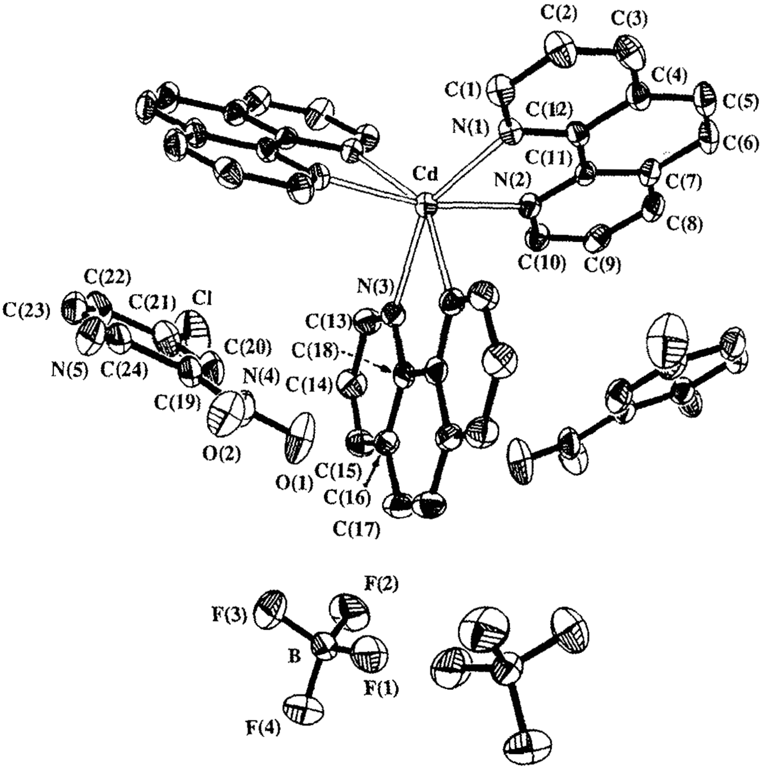

FIGURE 1 Structure and numbering scheme for [Cdphen$_3$](BF$_4$)$_2$·2CNA.

3.002Å, symmetry code: 0.5 + x, 0.5 + y, 0.5 − z) is observed between BF$_4^-$ anions and 4-chloro-2-nitrobenzenamine molecules, and which is a little stronger than that between the ClO$_4^-$ anion and the *para*-nitroaniline molecule in [Cdphen$_3$](ClO$_4$)$_2$·2CNA (O···H-N 3.054(7) and 3.097(8)Å). Furthermore, there is an intramolecular hydrogen bond in the 4-chloro-2-nitro-benzenamine molecule [N(5)-H(5b)···O(2) 2.613Å], which is stronger than intermolecular hydrogen bonds in [Cdphen$_3$](BF$_4$)$_2$·2CNA.

IR Spectra and Thermogravimetric Analysis

In the $\gamma_{\text{N-H}}$ region of the IR spectrum of [Cdphen$_3$](BF$_4$)$_2$·2CNA, the two sharp bands around 3490 and 3375 cm^{-1} assigned to the N-H group of 4-chloro-2-nitrobenzenamine, are shifted to higher frequencies by *ca* 24 and 25 cm^{-1} respectively, as compared with the standard IR spectra of 4-chloro-2-nitrobenzenamine. This indicates that the intramolecular hydrogen bonds in 4-chloro-2-nitrobenzenamine molecules in [Cdphen$_3$](BF$_4$)$_2$·2CNA are slightly weaker than those in pure 4-chloro-2-nitrobenzenamine. A strong and broad band at

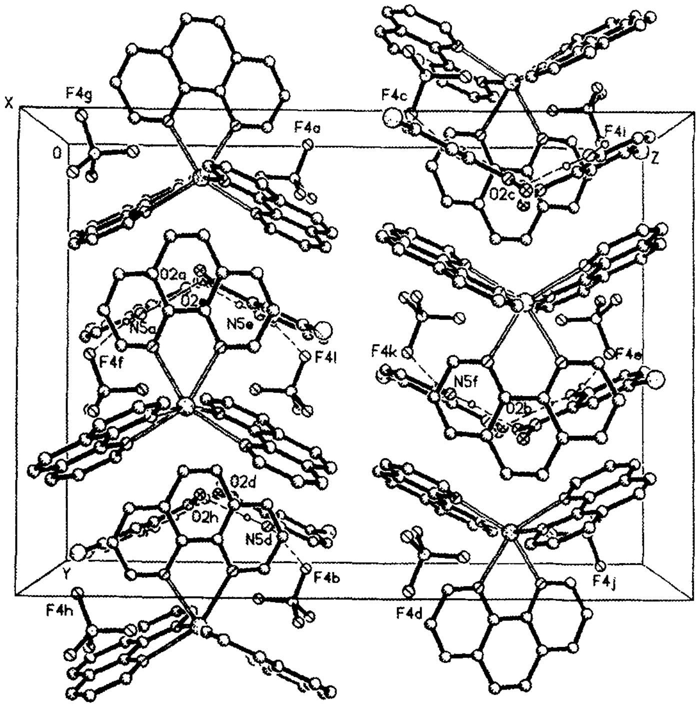

FIGURE 2 Unit cell molecular packing of [Cdphen$_3$](BF$_4$)$_2$·2CNA viewed down the *a* axis.

1059 cm^{-1} is mainly attributed to the tetrafluoroborate groups, indicating that the tetrafluoroborate is not coordinated to cadmium [10]. In the far-IR spectrum, several bands at 418, 276, 241 cm^{-1} along with 191, 172, 155 cm^{-1} are in good agreement with others in $(L)_3Cd(BF_4)_2{\cdot}H_2O$ (L=*bis*(4-methylpyrozyl-1-methane) [10].

Thermogravimetric analysis (TGA) of $[Cdphen_3](BF_4)_2{\cdot}2CNA$ revealed that the first decomposition event is centred at 204°C, a lower temperature with respect to $[Cdphen_3](ClO_4)_2{\cdot}2PNA$ (247°C). This suggests that the thermal stability of $[Cdphen_3](BF_4)_2{\cdot}2CNA$ is slightly less than that of $[Cdphen_3](ClO_4)_2{\cdot}2PNA$, even though $[Cdphen_3](BF_4)_2{\cdot}2CNA$ is thermally stable. According to the weight changes, the first weight loss (28.9%) corresponds to the loss of two 4-chloro-2-nitrobenzenamine molecules (calc. 29.4%), and is endothermic.

SUPPLEMENTARY MATERIAL

H atom positions, thermal parameter and lists of observed and calculated structures are available from the authors on request.

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