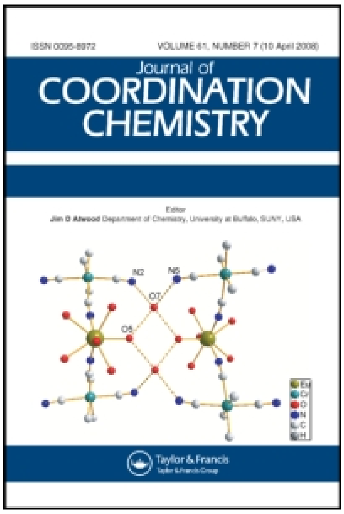

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Supramolecular Assemblies *via* Hydrogen Bonding and π-π Stacking Interactions: Crystal Structures of [Co(phen)(H_2O)$_4$]L·0.5H_2O and [CO_2(phen)$_2$(H_2O)$_2$$L_2$] with H_2L = Adipic Acid

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SUPRAMOLECULAR ASSEMBLIES *VIA* HYDROGEN BONDING AND π–π STACKING INTERACTIONS: CRYSTAL STRUCTURES OF $[Co(phen)(H_2O)_4]L \cdot 0.5H_2O$ AND $[CO_2(phen)_2(H_2O)_2L_2]$ WITH H_2L = ADIPIC ACID

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Reaction of freshly-prepared $CoCO_3$, phenanthroline monohydrate and adipic acid (H_2L) in CH_3OH/H_2O produced a mixture of $[Co(phen)(H_2O)_4]L \cdot 0.5H_2O$ (**1**) and $[CO_2(phen)_2(H_2O)_2L_2]$ (**2**). Complex **1** crystallizes in the orthorhombic space group *Pbcn* with cell dimensions $a = 23.380(2)$, $b = 12.347(1)$, $c = 12.821(1)$ Å, and $D_{calc} = 1.390\,g/cm^3$ for $Z = 8$, and complex **2** in the triclinic space group $P\bar{1}$ with cell dimensions $a = 8.203(1)$, $b = 9.809(1)$, $c = 11.827(1)$ Å, $\alpha = 70.34(1)$, $\beta = 74.81(1)$, $\gamma = 71.54(1)^\circ$ and $D_{calc} = 1.592\,g/cm^3$ for $Z = 1$. Complex **1** consists of $[Co(phen)(H_2O)_4]^{2+}$ complex cations, adipate anions and crystal H_2O molecules. The Co atoms are each octahedrally coordinated by one chelating phen ligand and four water molecules with $d(Co–O) = 2.041–2.097$ Å and $d(Co–N) = 2.144$, 2.160 Å. Through hydrogen bonds, the $[Co(phen)(H_2O)_4]^{2+}$ complex cations and adipate anions are interconnected into 2D layers, whose assembly could be ascribed to weak π–π stacking interactions between interdigitating phen ligands. Complex **2** is composed of centrosymmetric dinuclear $[Co_2(phen)_2(H_2O)_2L_2)$ molecules, in which the Co atoms are each coordinated by two N atoms of one chelating phen ligand and four O atoms of one H_2O molecule and two adipato ligands to form distorted octahedra with $d(Co–O) = 2.027–2.248$ Å and $d(Co–N) = 2.112$, 2.162 Å. The centrosymmetric molecules are assembled *via* intermolecular hydrogen bonds and π–π interactions into 2D layers.

Keywords: Cobalt(II); Phen complexes; Adipato complexes; Crystal structures; Hydrogen bonding; π–π stacking

INTRODUCTION

Self-assembly based on metal ligand coordination bonds, π–π stacking interactions and hydrogen bonds provides an efficient route to supramolecular architectures with specific topologies [1–4]. In particular, π–π stacking interactions between aromatic rings are recognized to be very important in proteins and protein–DNA systems for protein stabilization and various regulatory processes [5–7]. On the other hand, hydrogen bonds play vital roles in biological reactions and are essential for molecular recognition and self-organization of molecules in supramolecular chemistry.

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Furthermore, hydrogen-bond assembled molecular materials are of considerable interest with the incorporation of a transition metal ion in crystal engineering of materials [8].

Our recent interest has focussed on the self-assembly of transition metals with flexible α,ω-dicarboxylate anions. Previous investigations show α,ω-dicarboxylate anions to be versatile bridging ligands. For example, adipate anions in $Mg(H_2O)_4(C_6H_8O_4)$, $Cu(H_2O)_2(C_6H_8O_4)$ and $[(H_2O)_4Co(\mu\text{-}H_2O)_2Co(\mu\text{-}C_6H_8O_4)_{4/2}]\cdot 4H_2O$ serve as bis-monodentate ligands to bridge metal atoms [9–11]. In $Mn_2(H_2O)(C_6H_8O_4)_2$, the carboxylate group at one end chelates one Mn atom and both carboxyl O atoms at the other end are each coordinated to one Mn atom [12]. In $La_2(C_6H_8O_4)_3\cdot 10H_2O$ two crystallographically distinct adipato ligands are present [13], of which one bischelates two La atoms whereas the other functions similarly to that in $Mn_2(H_2O)(C_6H_8O_4)_2$. Incorporation of phenanthroline into the metal dicarboxylates could offer a series of mixed ligand metal complexes with new structure types [14–19]. As a continuation of our research, we report the self-assembly of cobalt with phenanthroline and adipate anions to produce two complexes $[Co(phen)(H_2O)_4]L\cdot 0.5H_2O$ (**1**) and $[CO_2(phen)_2(H_2O)_2L_2]$ (**2**). Their structures indicate that hydrogen bonds and π–π interactions are responsible for supramolecular assemblies.

EXPERIMENTAL

All chemical of p.a. grade were commercially available and used without further purification. C, H and N microanalyses were performed with a Heraeus Rapid-CHNO instrument. FT-IR spectra were recorded using KBr pellets in the range 4000–400 cm^{-1} on a Protege 460 spectrometer.

Synthesis

Addition of 3.0 cm^3 (1 M) aqueous Na_2CO_3 to an aqueous solution of 0.73 g (2.50 mmol) $Co(NO_3)_2\cdot 6H_2O$ in 5.0 cm^3 H_2O produced a rose-colored precipitate, which was then separated and washed with doubly-distilled water three times. The precipitate was then added to a solution of 0.50 g (2.5 mmol) phenanthroline monohydrate and 0.37 g (2.50 mmol) adipic acid dissolved in 40 cm^3 CH_3OH–H_2O (1 : 1 v/v) and stirred until complete dissolution occurred. The resulting orange solution ($pH = 6.26$) was then maintained at room temperature. Slow evarporation during two weeks afforded a mixture of $[Co(phen)(H_2O)_4]L\cdot 0.5H_2O$ (**1**) and $[Co(phen)_2(H_2O)_2L_2]$ (**2**) as major and minor products, respectively, which grew in the form of rose-colored prisms and red plate-like crystals. The major product $[Co(phen)(H_2O)_4]L\cdot 0.5H_2O$ (**1**) could be readily collected by hand-picking (Yield: *ca.* 57%). Anal. Calc. for $C_{18}H_{25}CoN_2O_{8.5}$ (%): C, 46.56; H, 5.42; N, 6.03. Found: C, 46.48; H, 5.60; N, 6.12. IR (cm^{-1}): 3261s, 1547vs, 1424vs, 1311s, 1226w, 1189w, 1134m, 1104w, 1091w, 1049w, 1006w, 929w, 854s, 813m, 789m, 728s, 644s, 422w.

X-Ray Crystallography

A fragment was cut from a bulky crystal of **1** and a plate-like crystal of **2** was selected. They were then glued on glass fibers with epoxy cement and later mounted on a

Bruker P4 diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) for cell determination and data collection. Lattice parameters were refined from 2ϑ values (10–25°) of 25 carefully centered reflections and reflection intensities were collected at 293 K using the ϑ–2ϑ scan technique. Corrections for Lorentz polarization and absorption effects were performed on the basis of ψ-scans. The structures were solved by direct methods using SHELXS-97 [20]. Subsequent difference Fourier syntheses enabled all nonhydrogen atoms to be located. After several cycles of refinement, the hydrogen atoms associated with C atoms were added in calculated positions and the ordered water hydrogen atoms were derived from successive difference Fourier syntheses. No attempt has been made to locate hydrogen atoms of the partially occupied water molecule in complex **1**. Final full-matrix least squares refinement using SHELXL-97 [21] converged very well with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms. Crystal data, intensity collection and structure refinement details are summarized in Table I; final atomic positional parameters, selected interatomic distances and bond angles are given in Tables IIA,B and Table III, respectively.

TABLE I Crystal data and structure refinement details for $[Co(phen)(H_2O)_4]L \cdot 0.5H_2O$ (**1**) and $[CO_2(phen)_2(H_2O)_2L_2]$ (**2**)

Compounds	**1**	**2**
Color/shape	Rose-colored/prisms	Red/thin plates
Size (mm)	0.889 × 0.600 × 0.444	0.222 × 0.178 × 0.067
Empirical formula	$C_{18}H_{25}CoN_2O_{8.5}$	$C_{36}H_{36}Co_2N_4O_{10}$
Formula weight	464.33	802.55
Temperature	293 K	293 K
Crystal system	Orthorhombic	Triclinic
Space group	*Pbcn*	$P\bar{1}$
No. of reflections used for unit cell determination (2θ range)	25 (10.0–25.0°)	25 (10.0–25.0°)
a, Å	23.380(2)	8.203(1)
b, Å	12.347(1)	9.809(1)
c, Å	15.376(1)	11.827(1)
α, deg		70.34(1)
β, deg		74.81(1)
γ, deg		71.54(1)
Volume (Å^3)	4438.6(8)	837.1(2)
Z	8	1
D_{calc} (g/cm^3)	1.390	1.592
μ(MoK_α) (cm^{-1})	8.20	10.58
$F(000)$	1936	414
Diffractometer	Bruker P4	
Radiation	MoK_α ($\lambda = 0.71073$ Å), graphite monochromated	
Scan type	θ–2θ	
$2\theta_{max}$	55°	55°
No. of reflections measured	Total: 6211; unique: 5069 ($R_{int} = 0.0393$)	Total: 4609; unique: 3813 ($R_{int} = 0.0342$)
Correction	Lp and empirical absorption	
Structure solution	Direct methods (SHELXS-97) [20]	
Refinement	Full-matrix least-squares (SHELXL-97) [21]	
No. observations ($I \geq 2\sigma(I)$)	4161	2596
No. variables	274	246
Residuals: R_1; wR_2[a]	0.0692; 0.1634	0.0536, 0.0914
S	1.253	1.029
Max. peak in final diff. Map	1.489 e/Å^3	0.400 e/Å^3

[a] $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$.

Crystallographic data including structure factors are available from the authors upon request (CCDC nos. 169512 and 169513 for 1 and 2, respectively).

RESULTS AND DISCUSSION

[Co(phen)(H_2O)$_4$]L · 0.5H_2O (1)

The crystal structure of **1** is composed of $[Co(phen)(H_2O)_4]^{2+}$ complex cations, adipate anions ($L^{2-} = (C_6H_8O_4)^{2-}$) and crystal H_2O molecules. Within the divalent complex cations (Fig. 1a), the Co atoms are each surrounded by two N atoms of one chelating phen ligand and four O atoms of different H_2O molecules to complete distorted octahedral coordination with d(Co–O) = 2.041–2.097 Å and d(Co–N) = 2.144, 2.160 Å (Table III). Through the strong hydrogen bonds formed between the coordinating water and the carboxyl O atoms with $d(O\text{–}H\cdots O) = 2.612 - 2.768A$ and $\angle(O\text{–}H\cdots O) = 149\text{–}173^\circ$ (Table III), each complex cation is surrounded by six adipate anions, which are each in turn hydrogen bonded to six complex cations as shown in Fig. 1a. As a result, hydrogen-bonded 2D layers consisting of the complex cations and adipate

TABLE IIA Atomic parameters and equivalent isotropic thermal parameters (Å^2) for nonhydrogen atoms in [Co(phen)(H_2O)$_4$]L · 0.5H_2O (**1**). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
Co	0.82368(1)	0.96025(2)	0.35087(2)	0.0311(2)
N(1)	0.8630(1)	0.8034(2)	0.3536(1)	0.0384(5)
N(2)	0.9135(1)	0.9981(2)	0.3638(2)	0.0497(6)
C(1)	0.8374(2)	0.7081(2)	0.3481(2)	0.0468(7)
C(2)	0.8675(2)	0.6097(3)	0.3506(2)	0.0609(9)
C(3)	0.9249(2)	0.6122(3)	0.3587(3)	0.075(1)
C(4)	0.9534(2)	0.7107(3)	0.3652(3)	0.068(1)
C(5)	1.0148(2)	0.7238(5)	0.3723(4)	0.101(2)
C(6)	1.0394(2)	0.8193(5)	0.3772(4)	0.100(2)
C(7)	1.0072(2)	0.9166(4)	0.3753(3)	0.073(1)
C(8)	1.0309(2)	1.0203(5)	0.3807(4)	0.091(1)
C(9)	0.9971(2)	1.1079(4)	0.3780(3)	0.092(1)
C(10)	0.9379(2)	1.0951(3)	0.3684(3)	0.073(1)
C(11)	0.9474(1)	0.9099(3)	0.3669(2)	0.0498(7)
C(12)	0.9204(1)	0.8058(3)	0.3620(2)	0.0458(6)
C(13)	0.8327(1)	1.2486(2)	0.1534(2)	0.0366(6)
C(14)	0.8393(2)	1.3431(2)	0.0914(2)	0.0446(6)
C(15)	0.8302(1)	1.4534(2)	0.1316(2)	0.0411(6)
C(16)	0.8327(1)	1.5454(2)	0.0660(2)	0.0399(6)
C(17)	0.8187(1)	1.6539(2)	0.1069(2)	0.0394(6)
C(18)	0.8146(1)	1.7486(2)	0.0448(2)	0.0362(5)
O(1)	0.8414(1)	1.1553(1)	0.1246(1)	0.0490(5)
O(2)	0.8188(1)	1.2672(2)	0.2302(1)	0.0689(8)
O(3)	0.8164(1)	1.8418(1)	0.0748(1)	0.0512(6)
O(4)	0.8097(2)	1.7298(2)	− 0.0344(1)	0.0750(9)
O(5)	0.7990(1)	1.1188(1)	0.3481(1)	0.0436(5)
O(6)	0.7405(1)	0.8991(2)	0.3445(1)	0.0397(4)
O(7)	0.8127(1)	0.9671(1)	0.4861(1)	0.0472(5)
O(8)	0.8268(1)	0.9683(1)	0.2157(1)	0.0491(6)
O(9)*	0.9084(4)	1.3521(6)	0.3496(4)	0.101(2)

*$S.O.F = 0.5$.

TABLE IIB Atomic parameters and equivalent isotropic thermal parameters (Å^2) for nonhydrogen atoms in $[Co_2(phen)_2(H_2O)_2L_2]$ (**2**). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x/a	y/b	z/c	U_{eq}
Co	0.57413(1)	0.65084(5)	0.78661(4)	0.0287(2)
N(1)	0.7262(3)	0.5037(3)	0.6746(2)	0.0310(6)
N(2)	0.4782(3)	0.7569(3)	0.6209(2)	0.0308(6)
C(1)	0.8473(4)	0.3776(4)	0.7024(3)	0.0380(8)
C(2)	0.9403(5)	0.2948(4)	0.6193(4)	0.048(1)
C(3)	0.9051(5)	0.3453(4)	0.5037(4)	0.049(1)
C(4)	0.7762(5)	0.4779(4)	0.4700(3)	0.0371(8)
C(5)	0.7261(6)	0.5391(5)	0.3521(3)	0.050(1)
C(6)	0.6029(6)	0.6676(5)	0.3247(3)	0.050(1)
C(7)	0.5157(5)	0.7491(4)	0.4130(3)	0.0400(9)
C(8)	0.3861(5)	0.8825(4)	0.3911(3)	0.051(1)
C(9)	0.3057(5)	0.9497(4)	0.4818(3)	0.050(1)
C(10)	0.3547(5)	0.8832(4)	0.5963(3)	0.0403(9)
C(11)	0.5581(4)	0.6906(4)	0.5305(3)	0.0300(7)
C(12)	0.6900(4)	0.5538(4)	0.5594(3)	0.0297(7)
C(13)	0.8445(4)	0.6789(3)	0.8305(3)	0.0295(7)
C(14)	0.9913(4)	0.6978(4)	0.8732(3)	0.342(8)
C(15)	0.9252(4)	0.7642(4)	0.9818(3)	0.0346(8)
C(16)	0.8069(4)	0.9213(3)	0.9534(3)	0.0344(8)
O(1)	0.7920(3)	0.7650(2)	0.7351(2)	0.0408(6)
O(2)	0.7722(3)	0.5740(2)	0.8947(2)	0.0361(6)
O(3)	0.5946(3)	1.1875(3)	1.1393(2)	0.0494(7)
O(4)	0.6020(4)	1.2160(3)	0.9437(2)	0.0576(8)
O(5)	0.4346(4)	0.4946(3)	0.8785(2)	0.0343(6)

anions are formed parallel to (100) with 1D tunnels extending along the [010] direction. The chelating phen ligands on both sides are nearly perpendicular to the 2D layers (Fig. 1b) and exhibit perfect coplanarity. All nonhydrogen atoms of the adipate anion are practically in a common plane. C–O bond lengths range from 1.241–1.251 Å and C–C bond lengths from 1.511–1.521 Å. The void space between the neighboring phen ligands on the same side of one 2D layer is filled by a phen ligand from an adjacent 2D layer. The mean interplanar distance between the interdigitating phen ligands is 3.78 Å indicating weak interlayer π–π stacking interactions [22–24]. According to the above description, it is clear that the hydrogen bonds are responsible for the supramolecular assembly of the complex cations and the adipate anions into 2D layers and the π–π stacking interactions for the interdigitation of the phen ligands of the 2D layers (Fig. 1b). The disordered crystal H_2O molecules donate their hydrogen atoms to carboxyl oxygen atoms, namely O(2) and O(4) (x, $-y+3$, $z+1/2$), to form weak hydrogen bonds with $d(\text{O–H}\cdots\text{O}) = 2.977, 3.085$ Å.

$[CO_2(phen)_2(H_2O)_2L_2]$ (2)

Replacement of three water O atoms within the $[Co(phen)(H_2O)_4]^{2+}$ complex cation in **1** by three carboxyl O atoms of two adipate anions (L^{2-}) results in significantly distorted $[CoN_2O_4]$ octahedral coordination in **2**. As illustrated in Fig. 2, the adipate anions bridge Co atoms into dinuclear $[Co_2(phen)_2(H_2O)_2L_2]$ complexes with the terminal carboxyl groups acting as both chelates and monodentates. Co–O bond distances to the chelating carboxyl O atoms are 2.123 and 2.248 Å, substantially longer than those of 2.027, 2.044 Å to the water O atom and the monodentate carboxyl O atom; Co–N

TABLE III Selected interatomic distances (Å) and bond angles (°) for (**1**) and (**2**)

$[Co(phen)(H_2O)_4]L \cdot 0.5H_2O$ (**1**)					
Co–O(5)	2.041(2)	Co–N(2)	2.160(3)	C(15)–C(16)	1.521(4)
Co–O(6)	2.089(2)	C(13)–O(1)	1.251(3)	C(16)–C(17)	1.515(3)
Co–O(7)	2.097(2)	C(13)–O(2)	1.245(3)	C(17)–C(18)	1.512(3)
Co–O(8)	2.082(2)	C(13)–C(14)	1.515(3)	C(18)–O(3)	1.241(3)
Co–N(1)	2.144(2)	C(14)–C(15)	1.511(4)	C(18)–O(4)	1.245(3)
O(5)–Co–O(6)	94.7(1)	O(6)–Co–O(8)	90.1(1)	O(8)–Co–N(1)	92.7(1)
O(5)–Co–O(7)	87.0(1)	O(6)–Co–N(1)	94.2(1)	O(8)–Co–N(2)	92.8(1)
O(5)–Co–O(8)	86.8(1)	O(6)–Co–N(2)	171.0(1)	N(1)–Co–N(2)	77.2(1)
O(5)–Co–N(1)	171.1(1)	O(7)–Co–O(8)	172.9(1)	O(1)–C(13)–O(2)	123.2(2)
O(5)–Co–N(2)	94.0(1)	O(7)–Co–N(1)	93.6(1)	O(3)–C(18)–O(4)	122.7(2)
O(6)–Co–O(7)	87.0(1)	O(7)–Co–N(2)	91.1(1)		
Hydrogen bonding contacts					
D–H	d(D–H)	$d(H \cdots A)$	$\angle(D–H \cdots A)$	$d(D–H \cdots A)$	A
O(5)–H(5a)	0.932	1.703	167	2.619	O2
O(5)–H(5b)	0.939	1.698	163	2.612	O4 [$x, -y+3, z+1/2$]
O(6)–H(6a)	0.912	1.945	149	2.768	O2 [$-x+3/2, y-1/2, z$]
O(6)–H(6b)	0.769	1.958	168	2.716	O4 [$-x+3/2, -y+5/2, z+1/2$]
O(7)–H(7a)	0.839	1.931	151	2.696	O1 [$x, -y+2, z+1/2$]
O(7)–H(7b)	0.781	2.004	154	2.726	O3 [$x, -y+3, z+1/2$]
O(8)–H(8a)	0.712	1.996	162	2.681	O3 [$x, y-1, z$]
O(8)–H(8b)	0.815	1.912	173	2.723	O1
$[CO_2(phen)_2(H_2O)_2L_2]$ (2)					
Co–O(1)	2.248(2)	Co–N(2)	2.112(2)	C(15)–C(16)	1.519(4)
Co–O(2)	2.123(2)	C(13)–O(1)	1.247(3)	C(16)–C(17)	1.514(4)
Co–O(3)^{1}	2.027(2)	C(13)–O(2)	1.269(4)	C(17)–C(18)	1.513(4)
Co–O(5)	2.044(3)	C(13)–C(14)	1.504(4)	C(18)–O(3)	1.257(4)
Co–N(1)	2.162(2)	C(14)–C(15)	1.530(4)	C(18)–O(4)	1.240(4)
O(1)–Co–O(2)	59.7(1)	O(2)–Co–O(5)	99.1(1)	O(5)–Co–N(1)	87.8(1)
O(1)–Co–O(3)^{I}	92.4(1)	O(2)–Co–N(1)	90.6(1)	O(5)–Co–N(2)	104.3(1)
O(1)–Co–O(5)	158.7(1)	O(2)–Co–N(2)	153.1(1)	N(1)–Co–N(2)	77.3(1)
O(1)–Co–N(1)	89.7(1)	O(3)^{1}–Co–O(5)	94.5(1)	O(1)–C(13)–O(2)	120.0(3)
O(1)–Co–N(2)	95.8(1)	O(3)^{1}–Co–N(1)	167.8(1)	O(3)–C(18)–O(4)	125.7(3)
O(2)–Co–O(3)^{I}	100.8(1)	O(3)^{1}–Co–N(2)	90.5(1)		
Hydrogen bonding contacts					
D–H	d(D–H)	$d(H \cdots A)$	$\angle(D–H \cdots A)$	$d(D–H \cdots A)$	A
O(5)–H(5a)	0.808	2.031	151	2.766	O2 [$-x+1, -y+1, -z+2$]
O(5)–H(5b)	0.864	1.764	159	2.591	O4 [$x, y-1, z$]

Symmetry code: I: $1-x, 2-y, 2-z$.

bond distances are 2.112 and 2.162 Å (Table III). The resulting dinuclear molecules are centered at the crystallographic 1*d* position. The chelating phen ligands exhibit nearly perfect coplanarity and coordinating H_2O molecules donate hydrogen atoms to the coordinating and noncoordinating carboxyl O atoms of different adipato ligands of neighboring complex molecules to form strong intermolecular hydrogen bonds with $d(O–H \cdots O) = 2.591$, 2.766 Å and $\angle(O–H \cdots O) = 159$, 151° (Table III). Due to such bonds, the centrosymmetric dimers are connected into 1D chains along [010].

Interdigitation of the chelating phen ligands of adjacent chains leads to formation of 2D layers parallel to (100) (Fig. 3). Interplanar distances between interdigitating

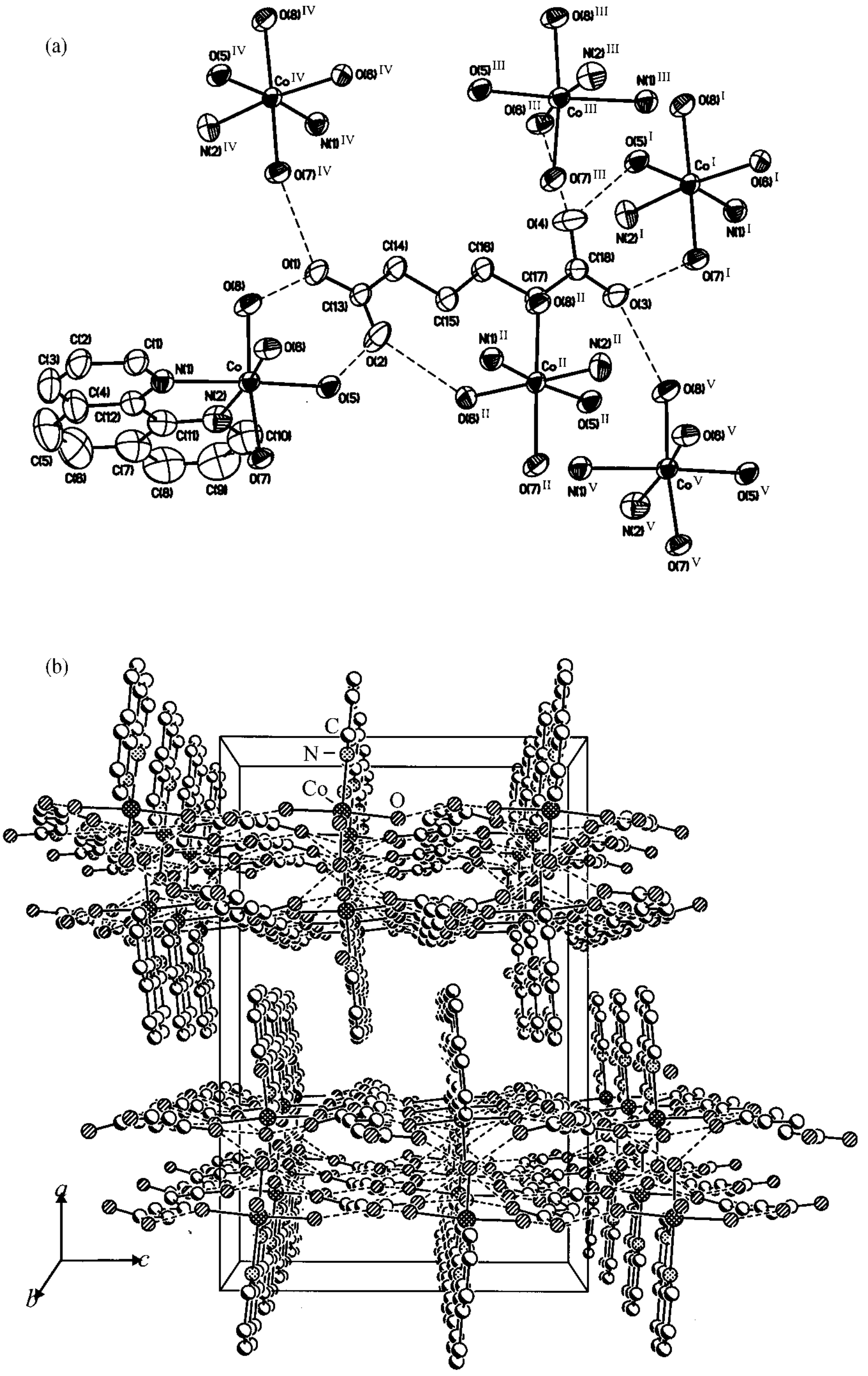

FIGURE 1 (a) ORTEP view of $[Co(phen)(H_2O)_4]^{2+}$ cations together with hydrogen bonded adipate anions with displacement ellipsoids (50% probability) and atomic labeling; (b) Perspective view of the crystal structure of $[Co(phen)(H_2O)_4]L \cdot 0.5H_2O$ (**1**) (symmetry codes are I: $x, -y+3, z-1/2$; II: $-x-1/2, y+3/2, z+1$; III: $-x+3/2, -y+5/2, z-1/2$; IV: $x, -y+2, z-1/2$; V: $x, y+1, z$).

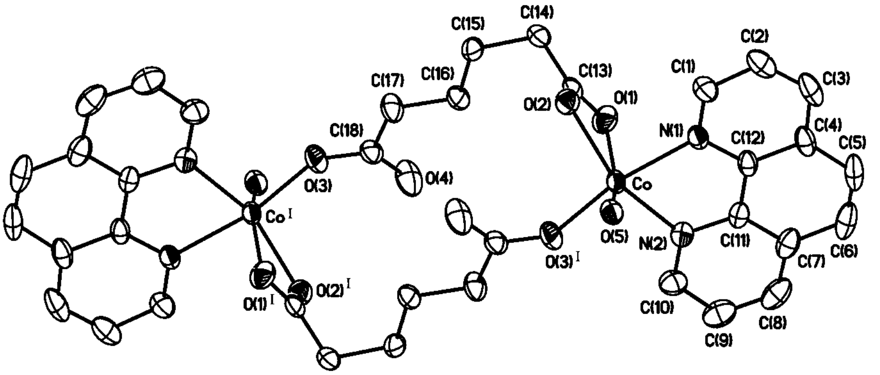

FIGURE 2 ORTEP view of a dinuclear $[Co_2(phen)_2(H_2O)_2L_2]$ complex with displacement ellipsoids (50% probability) and atomic labeling.

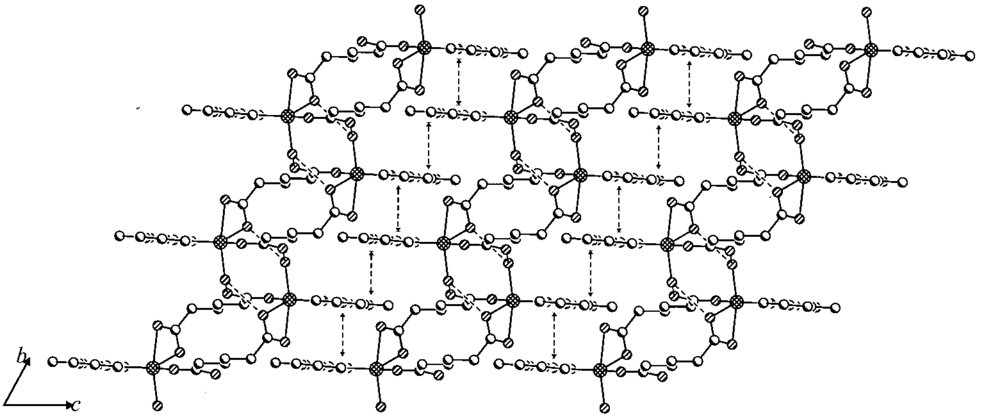

FIGURE 3 Supramolecular assembly of the dinuclear $[Co_2(phen)_2(H_2O)_2L_2]$ molecules *via* intermolecular hydrogen bonds (dashed lines) and π–π stacking interactions (dashed double arrows).

phen ligands are 3.43 Å on average, suggesting significant intermolecular π–π stacking interactions [22–24].

CONCLUSION

It is clear now that both intermolecular hydrogen bonds and π–π stacking interactions are responsible for the supramolecular assemblies of the dinuclear complex molecules. In contrast to the adipate anions in complex **1**, the adipato ligands in **2** are twisted with a torsion angle of 63.6(4)° for the C13–C14–C15–C16 chain, all nonhydrogen atoms except the chelating –COO carboxyl group being in a common plane. The present bridging mode of the adipato ligands is significantly different to those observed in $Cu(H_2O)_2(C_6H_8O_4)$ [10], $[(H_2O)_4Co(\mu\text{-}H_2O)_2Co(\mu\text{-}C_6H_8O_4)_{4/2}]\cdot 4H_2O$ [11], $Mn_2(H_2O)(C_6H_8O_4)_2$ [12] and $La_2(C_6H_8O_4)_3\cdot 10H_2O$ [13], where the adipto ligands interlink metal atoms to form coordination polymers.

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