

CHAPTER 2

PREPARATION AND CHARACTERIZATION OF BIS(1,2–DIAMINOETHANE) COBALT(II) HEXAVANADATE: A LAYERED POLYOXOVANADATE PILLARED BY A COBALT COORDINATION COMPLEX

Polyoxovanadate frameworks (POVs) have been capturing broad interest from materials chemists primarily because of their technological potential, *e.g.*, as oxidative catalysts and secondary cathode materials for advanced lithium batteries [1, 2]. The inherent ability of vanadium atom to adopt various coordination geometries and oxidation states while being a good electron–acceptor and electron relay–station is also a driving force for the research in the field [3, 4]. Current interest regarding the preparation of POVs focuses on the introduction of a secondary metal, particularly a transition metal to the coordinate covalent POV frameworks. Cobalt is unique in its coordination chemistry, redox activity and potential magnetic functionality, and therefore has been one of the most studied secondary metals. Although there are earlier reports on the successful introduction of cobalt into POV frameworks (Co–POV) *e.g.* $[\text{Co}(2,2'\text{-bpy})_2]_2[\text{As}_8\text{VO}_{42}(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ [5], $[\text{Co}(\text{en})_2(\text{H}_2\text{O})]\{[\text{Co}(\text{en})_2]\text{As}_8\text{V}_{14}\text{O}_{42}(\text{SO}_4)\} \cdot 3\text{H}_2\text{O}$ [6], $[\text{Co}(\text{Hdpa})_2\text{V}_4\text{O}_{12}]$ [7], $\text{Co}_2(4,4'\text{-bipy})_2(\text{V}_4\text{O}_{12})$ [8] and $\{[\text{H}_2(\text{en})]\text{Co}(\text{ox})(\text{V}_4\text{O}_{12})\}_n$ [9], none of these are the

Co-POV structures in which the cobalt complex present as a pillaring unit. Examples of POV frameworks where the secondary metal acts as a pillaring motif between the POV sheets are very few, $(\text{C}_2\text{N}_2\text{H}_8)_2\text{Zn}[\text{V}_6\text{O}_{14}]$, $(\text{C}_2\text{N}_2\text{H}_8)_2\text{Cu}[\text{V}_6\text{O}_{14}]$, $[\text{Ni}(\text{C}_2\text{N}_2\text{H}_8)_2]_{0.5}[\text{V}_3\text{O}_7]$ and $[\text{Ni}(\text{en}-\text{Me})_2]_{0.5}[\text{H}_2\text{enMe}]_{0.5}[\text{V}_6\text{O}_{14}]$ [10, 11]. In this chapter, we report the preparation and crystal structure of $\text{Co}^{\text{II}}(\text{C}_2\text{N}_2\text{H}_8)_2[\text{V}_4^{\text{IV}}\text{V}_2^{\text{V}}\text{O}_{14}]$, which is the first example of a layered POV pillared by cobalt complex.

2.1 Experimental

2.1.1 Synthesis and initial characterization

Crystals of $\text{Co}^{\text{II}}(\text{C}_2\text{N}_2\text{H}_8)_2[\text{V}_4^{\text{IV}}\text{V}_2^{\text{V}}\text{O}_{14}]$ (**I**) were readily prepared from a reaction between $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98% Aldrich, 0.1006 g), V_2O_5 (99% Fluka, 0.2519 g) and ethylenediamine ($\text{C}_2\text{H}_8\text{N}_2$; en, 99% Fluka, 0.0719 g) in deionized water (2.80 cm^3) using a 17 cm^3 Teflon container. The reaction was conducted under autogenous pressure at 200 °C for 60 h before being cooled down to room temperature using a rather rapid rate of 0.5 °Cmin⁻¹. Black crystals of **I** were then separated from the supernatant solution by filtration, washed with deionized water and dried in air. The elemental composition in **I** was determined using the energy dispersive X-ray spectroscopic (EDS) microanalyzer equipped by the scanning electron microscope (FESEM, JEOLJSM-6335F) and a Perkin Elmer Series II 2400 CHN/S analyzer. Infrared spectra of also the ground crystals were collected on a Bruker Tensor 27 FT-IR instrument (4,000–400 cm^{-1} , resolution 0.5 cm^{-1}) using a KBr (BDH 98.5%) pellet. The X-ray powder diffraction (XRD) pattern was collected using a Bruker D8

Advance diffractometer, operating with a Ni filtered Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$, 48 kV and 30 mA).

2.1.2 Single crystal structure determination

In order to determine the crystal structure of **I**, a full set of intensity data was collected on a single crystal of size $0.20 \times 0.04 \times 0.04 \text{ mm}^3$ at 150(2) K using a Stöe IPDS2 image plate diffractometer operating with Mo $K\alpha$ radiation, employing a single ω -scan. The crystal was cooled using an Oxford Instruments nitrogen gas cryostream. The collected data were analytically corrected for absorption using the Tompa method [12]. The structure was then solved by direct methods implemented within SHELXS-97 [13] and full-matrix least squares refinement carried out within SHELXL-97 [14] via the WinGX program interface [15]. All non-hydrogen atoms were located from direct and difference Fourier maps and refined anisotropically. The hydrogen atoms in the en molecule were apparent from final difference Fourier maps, and were then placed and refined using a riding model with the following bond lengths: C-H 0.99(3) $\text{\AA}$; N-H 0.92(3) $\text{\AA}$.

2.2 Results and discussion

2.2.1 Structural description

The crystal structure of $\text{Co}^{\text{II}}(\text{C}_2\text{N}_2\text{H}_8)_2[\text{V}_4^{\text{IV}}\text{V}_2^{\text{V}}\text{O}_{14}]$ (**I**) was successfully solved and refined in the monoclinic space group $P2_1/n$ with the final refined cell parameters $a = 9.143(3) \text{ \AA}$, $b = 6.5034(11) \text{ \AA}$, $c = 15.874(4) \text{ \AA}$, $\beta = 101.90(2)^\circ$ and $V = 923.6(4) \text{ \AA}^3$. Details on the data collection and structure refinements are summarized in Table 2.1.

Table 2.1 Crystallographic data for structural solution and refinement of **I**.

Identification code	I
Empirical formula	$\text{Co}(\text{C}_2\text{N}_2\text{H}_8)_2[\text{V}_4^{\text{IV}}\text{V}_2^{\text{V}}\text{O}_{14}]$
Formula weight	708.78
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal size (mm^3)	$0.20 \times 0.049 \times 0.04$
$a/\text{\AA}$	9.143(3)
$b/\text{\AA}$	6.5034(11)
$c/\text{\AA}$	15.874(4)
$\beta/^\circ$	101.90(2)
volume/ $\text{\AA}^3$	923.6(4)
Z	2
T/K	150(2)
ρ_{calc} (g cm^{-3})	2.549
μ (mm^{-1})	3.854
θ range($^\circ$)	2.85–26.00
λ (Mo $K\alpha$) ($\text{\AA}$)	0.71069
R_{int}	0.0849
reflection collected	4591
unique reflections	1799
no. of parameters	134
R, R_w ($I > 2\sigma(I)$)	0.0399, 0.0652
R, R_w (all data)	0.0853, 0.0730
Goodness of fit	0.840

The ORTEP plot of the extended asymmetric unit showing the coordination environments of the structural building motifs and atomic numbering scheme is shown in Figure 2.1. The atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2.2.

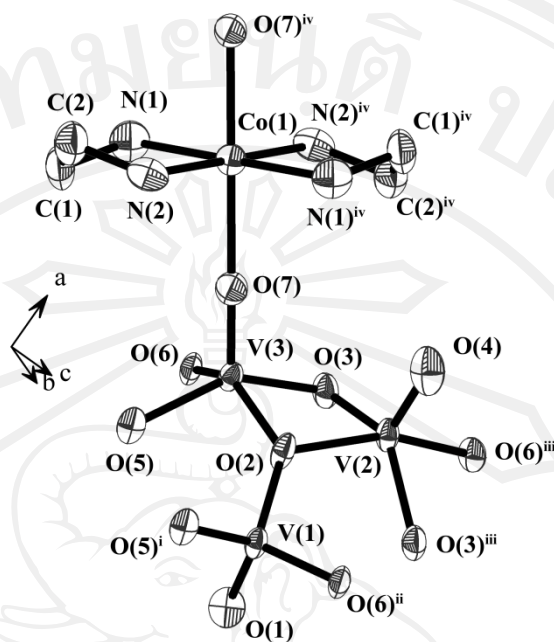


Figure 2.1 An ORTEP view of the extended asymmetric unit of **I** drawn at 80% probability level with hydrogen atoms omitted for clarity. Symmetry codes: (i) $[-x, -y + 2, -z]$ (ii) $[x, y + 1, z]$ (iii) $[-x + 0.5, y + 0.5, -z + 0.5]$ (iv) $[-x + 1, -y + 1, -z]$.

Table 2.2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) of non-hydrogen atoms for **I**.

	x	y	z	Ueq
V(1)	428(1)	12186(2)	930(1)	11(1)
V(2)	3260(1)	10000(2)	2331(1)	12(1)
V(3)	1932(1)	7190(2)	1008(1)	12(1)
O(1)	-1016(5)	11633(6)	1306(3)	20(1)
O(2)	1848(5)	10192(6)	1188(2)	15(1)
O(3)	2778(4)	7166(6)	2232(3)	15(1)
O(4)	4825(5)	10572(6)	2077(3)	24(1)
O(5)	77(5)	7489(5)	151(2)	14 (1)
O(6)	1161(4)	4589(6)	1384(2)	13(1)
O(7)	3237(5)	6607(6)	501(3)	18(1)
Co(1)	5000	5000	0	14(1)
N(1)	3691(6)	2363(8)	-417(3)	23(1)
N(2)	3993(6)	6049(8)	-1210(4)	19(1)
C(1)	2589(7)	2940(11)	-1201(4)	24(1)
C(2)	3322(8)	4276(10)	-1741(4)	24(1)

There are three crystallographically distinct sites of vanadium. The bond valence calculations based on a single point energy model, and refined bond distances listed in Table 2.3 can be calculated from equation 2.2.1 [16]:

$$V_j = \sum_{i=1}^N \exp \left[\frac{(R_0 - R_{ij})}{b} \right] \quad (2.2.1)$$

where, R_{ij} = related bond distances

R_0 = bond valence parameter (the bond length having a bond valence of 1)

b = the characteristic parameter of particular bond

The results suggest the presence of both pentavalent vanadium (V^V ; V(1)) and tetravalent vanadium (V^{IV} ; V(2), V(3)). Although the starting vanadium source is V_2O_5 , the mild reducing power of the organic component results in the mixed V^{IV}/V^V structure. The tetravalent V(2) and V(3) are characterized by square pyramidal geometry, $\{V^{IV}O_5\}_{sq}$, of 4 + 1 type, each of which shows four long equatorial bonds; V(2)–O(2), V(2)–O(3), V(2)–O(6), V(3)–O(2), V(3)–O(3), V(3)–O(5) and V(3)–O(6) in range 1.894(4)–2.017(4) Å with an average of 1.958(4) Å, and one short vanadyl bond, V(2)=O(4) (1.609(5) Å) and V(3)=O(7) (1.616(5) Å). The pentavalent V(1) on the other hand shows a 3 + 1 tetrahedral coordination, $\{V^VO_4\}_{tet}$, of which the bond lengths of the bridging V(1)–O(2) (1.821(4) Å), V(1)–O(5) (1.695(4) Å) and V(1)–O(6) (1.792(4) Å) bonds are longer than the terminal V(1)–O(1) (1.599(5) Å) bond. The distortion of the $\{V^VO_4\}_{tet}$ from the regular tetrahedron is apparent. The interatomic distances involving with the triply bridging oxygen, *i.e.* μ_3 –O(2) and μ_3 –O(6), are significantly longer than that of the doubly bridging oxygen, *i.e.* μ_2 –O(5).

The correlation between the refined bond distances and their corresponding polyhedral configurations agree well with the previously reported POV layer frameworks of the same composition and registry, *e.g.* $[\text{V}_6\text{O}_{14}](\text{C}_4\text{H}_{14}\text{N}_2)$, $[\text{V}_6\text{O}_{14}](\text{C}_5\text{H}_{16}\text{N}_2)$, $(\text{C}_2\text{N}_2\text{H}_8)_2\text{Zn}[\text{V}_6\text{O}_{14}]$ and $(\text{C}_2\text{N}_2\text{H}_8)_2\text{Cu}[\text{V}_6\text{O}_{14}]$ [10, 17].

Table 2.3 Selected bond distances and angles for compound **I**.

<i>Bond distances (Å)^a</i>			
V(1)–O(1)	1.599(5)	V(3)–O(3)	1.938(4)
V(1)–O(5) ⁱ	1.695(4)	V(3)–O(5)	1.953(4)
V(1)–O(6) ⁱⁱ	1.792(4)	V(3)–O(6)	1.972(4)
V(1)–O(2)	1.821(4)	V(3)–O(2)	1.976(4)
V(2)–O(4)	1.609(5)	Co(1)–O(7)	2.202(5)
V(2)–O(3)	1.894(4)	Co(1)–N(2) ^{iv}	2.067(5)
V(2)–O(3) ⁱⁱⁱ	1.908(4)	Co(1)–N(2)	2.067(5)
V(2)–O(2)	2.002(4)	Co(1)–N(1)	2.118(5)
V(2)–O(6) ⁱⁱⁱ	2.017(4)	Co(1)–N(1) ^{iv}	2.118(5)
V(3)–O(7)	1.616(5)		
<i>Bond angles (°)</i>			
O(1)–V(1)–O(5) ⁱ	109.4(2)	O(3)–V(3)–O(2)	83.23(16)
O(1)–V(1)–O(6) ⁱⁱ	108.4(2)	O(5)–V(3)–O(2)	87.06(15)
O(5) ⁱ –V(1)–O(6) ⁱⁱ	107.41(19)	O(6)–V(3)–O(2)	140.94(19)
O(1)–V(1)–O(2)	111.2(2)	O(7)–V(3)–O(5)	107.5(2)
O(5) ⁱ –V(1)–O(2)	110.46(19)	O(3)–V(3)–O(5)	144.03(19)
O(6) ⁱⁱ –V(1)–O(2)	109.93(18)	O(7)–V(3)–O(6)	107.23(19)
O(4)–V(2)–O(3)	114.1(2)	O(3)–V(3)–O(6)	77.49(17)
O(4)–V(2)–O(3) ⁱⁱⁱ	117.1(2)	O(5)–V(3)–O(6)	89.01(16)
O(3)–V(2)–O(3) ⁱⁱⁱ	128.64(9)	N(2) ^{iv} –Co(1)–N(2)	180.0
O(4)–V(2)–O(2)	101.5(2)	N(2) ^{iv} –Co(1)–N(1)	97.9(2)
O(3)–V(2)–O(2)	83.66(17)	N(2)–Co(1)–N(1)	82.1(2)
O(3) ⁱⁱⁱ –V(2)–O(2)	90.45(17)	N(1)–Co(1)–N(1) ^{iv}	180.0(3)
O(4)–V(2)–O(6) ⁱⁱⁱ	102.87(19)	N(2) ^{iv} –Co(1)–O(7)	92.31(19)
O(3)–V(2)–O(6) ⁱⁱⁱ	87.91(16)	N(2)–Co(1)–O(7)	87.69(19)
O(3) ⁱⁱⁱ –V(2)–O(6) ⁱⁱⁱ	77.08(16)	N(1)–Co(1)–O(7)	95.1(2)
O(2)–V(2)–O(6) ⁱⁱⁱ	155.62(18)	N(1) ^{iv} –Co(1)–O(7)	84.9(2)
O(7)–V(3)–O(3)	108.32(19)	O(7)–Co(1)–O(7) ^{iv}	180.00(19)
O(7)–V(3)–O(2)	111.0(2)		

^a Symmetry code: (i) $[-x, -y + 2, -z]$ (ii) $[x, y + 1, z]$ (iii) $[-x + 0.5, y + 0.5, -z + 0.5]$ (iv) $[-x + 1, -y + 1, -z]$.

Two adjacent $\{V^{IV}O_5\}_{sq}$ units share edges in a *trans* conformation to form a larger binuclear $\{V_2^{IV}O_8\}$ unit, which is then fused through *cis* edge sharing to the neighboring binuclear units to generate the $\{UuDd\}$ or $\{Z\}$ chain with a zigzag configuration as shown in Figure 2.2.

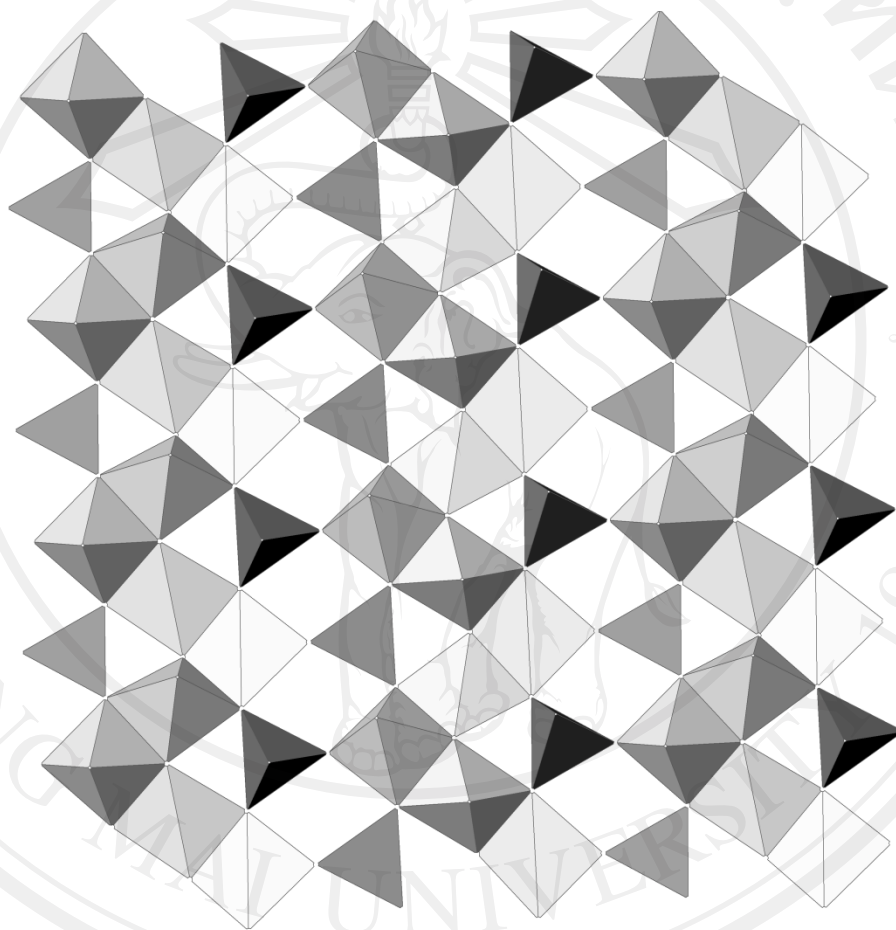


Figure 2.2 A polyhedral view of the $(\{UuDd\}:T.)\beta$ -POV layer in **I**.

Each chain is connected to the adjacent chains by the $\{V^{V}O_4\}_{tet}$, each of which share two basal corners with one chain and the other basal corner with the other chain. This results in a mixed valence $[V_4^{IV}O_{10}V_2^{V}O_4]^{2-}$ anionic layer of $\{UuDd\}:T.)\beta$ type in SP + T class and Z-T subclass [18]. These anionic POV layers extend parallel to the [101], and are linked further by the octahedral $\{Co^{II}O_2(C_2N_2H_8)_2\}$ pillars *via* the

two *trans* apical O(7) atoms of the $\{V^{IV}O_5\}_{sq}$ from two adjacent layers to generate a three-dimensional pillared Co–POV structure (Figure 2.3), which is isostructural with the zinc, copper and nickel analogues, $(C_2N_2H_8)_2Zn[V_6O_{14}]$, $(C_2N_2H_8)_2Cu[V_6O_{14}]$ and $[Ni(C_3N_2H_{11})_2]_{0.5}[C_3N_2H_{13}]_{0.5}[V_6O_{14}]$ [10, 11]. This implies the template function of the en and therefore the feasibility in crystal engineering of other analogous pillared structures.

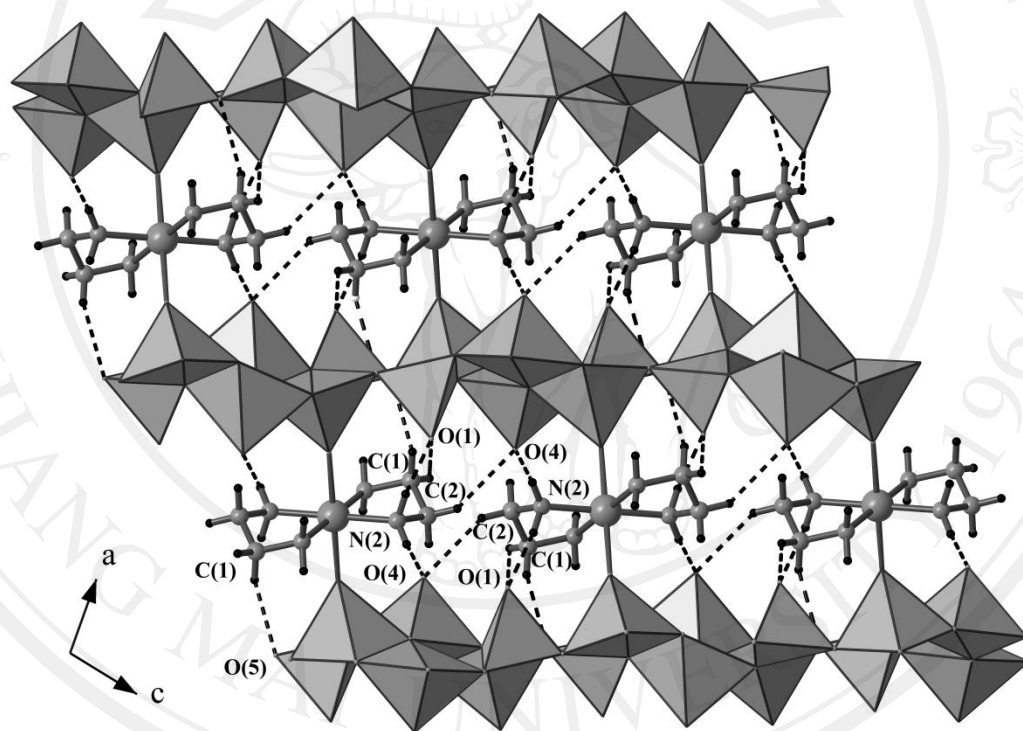


Figure 2.3 View of the 3-D structure of **I** with hydrogen bonds shown in dotted lines.

The pseudo-octahedral coordination of the cobalt is completed by four nitrogen atoms from two *trans* en ligands, locating about the inversion center at the cobalt atom. The bond valence calculations suggested the divalent state of the cobalt and therefore a dpositively charged $\{Co^{II}O_2(C_2N_2H_8)_2\}$ pillar, which consequently

balances the negatively charged POV layer. The framework of **I** is similar in some respects to that of $[\{\text{Co}(\text{pyz})\}(\text{V}_2\text{O}_5)_2]$, pyz = pyrazine [19], which has been reported recently. In **I**, the layers are linked by discrete $\text{Co}(\text{en})_2^{2+}$ units, but in $[\{\text{Co}(\text{pyz})\}(\text{V}_2\text{O}_5)_2]$ layers are linked by a series of 1-D chains of formulation $\{\text{Co}(\text{pyz})\}^{2+}$. However, a different POV layer of type 2($\{\text{UDD}\}$) is present within $[\{\text{Co}(\text{pyz})\}(\text{V}_2\text{O}_5)_2]$.

The analysis of hydrogen bonding interactions as listed in Table 2.4 suggests the spatial arrangement of the en to be partially imparted by the hydrogen bonds established between both the polar nitrogen atoms and the methylene carbon atoms of the organic molecule, and the vanadyl oxygen atoms of the POV layer, *i.e.* N–H $\cdots$ O and C–H $\cdots$ O. Although the established C–H $\cdots$ O hydrogen bonds are very weak [20], they may play a part in synergistic with the octahedral coordination geometry of the Co^{II} ion, in regulating the spatial arrangement of the en in relative to the POV layer. It is apparent in Figure 2.3 that the en acting as a bidentate ligand are arranged roughly in a plane parallel to the POV layers, which is also the case for the analogous $(\text{C}_2\text{N}_2\text{H}_8)_2\text{Zn}[\text{V}_6\text{O}_{14}]$ and $(\text{C}_2\text{N}_2\text{H}_8)_2\text{Cu}[\text{V}_6\text{O}_{14}]$ structures [17].

Table 2.4 Hydrogen bonding geometry for **I**.

D – H $\cdots$ A ^a	D – H, (Å)	H $\cdots$ A, (Å)	D $\cdots$ A, (Å)	D – H $\cdots$ A, (°)
N(2) – H(2C) $\cdots$ O(1) ⁱ	0.92	2.21	3.088(7)	159
N(2) – H(2D) $\cdots$ O(4) ^v	0.92	2.12	2.916(7)	144
C(1) – H(1A) $\cdots$ O(1)	0.99	2.47	3.293(8)	140
C(1) – H(1B) $\cdots$ O(5) ^{vi}	0.99	2.51	3.237(9)	130
C(2) – H(2A) $\cdots$ O(4) ^{vii}	0.99	2.54	3.359(8)	140

^a Symmetry code: (i) $[-x, -y + 2, -z]$ (v) $[-x + 1, -y + 2, -z]$ (vi) $[-x, -y + 1, -z]$ (vii) $[x - 0.5, -y + 1.5, z - 0.5]$.

Elemental analysis of ground crystals using an energy dispersive X-ray spectroscopic (EDS) microanalyzer confirms the crystallographically observed ratio of 1:6 for Co:V. CHNS analysis data of bulk samples fit rather poorly to the crystallographically observed formulation [*found*; C 46.61%, N 39.97%, H 13.42%; *calculated*; C 50.04%, N 39.45%, H 10.50%]. The data suggest impurities are present, possibly with coordinated water. However, the X-ray powder diffraction data show that the pillared phase is the dominant crystalline component present in the bulk as shown in Figure 2.4.

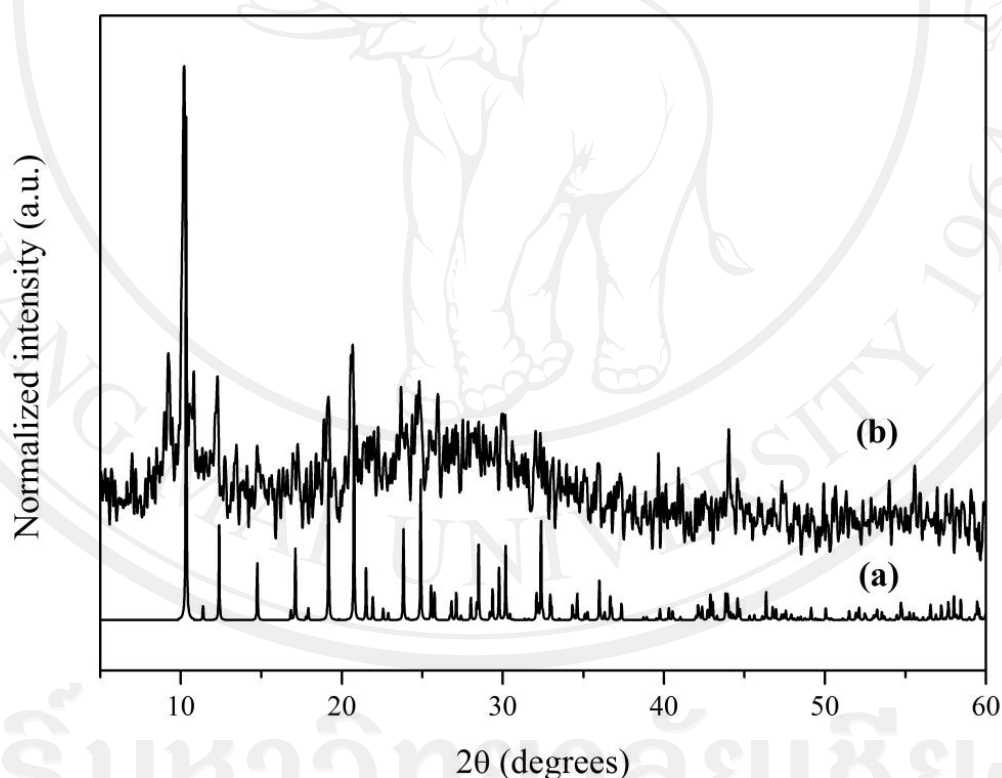


Figure 2.4 Powder X-ray diffraction pattern of compound **I** (a) simulated (b) experimental XRD patterns.

2.2.2 FT – IR spectra of compound I

FT–IR spectrum is shown in Figure 2.5 and reveals the existence of the major functional groups of the en and the atoms ligated to the cobalt; 3452vs, 3015vs (ν (N–H; NH₂)); 1630s (δ (N–H)); 1463m (δ (C–H; CH₂)); 1055m (ν (C–N)); 973s (ν (V–O_i)); 740s (ν (V–O_b)); 673m (ν (Co–N)); 465m (ν (Co–O)). The broadening effect is also observed in the spectrum which is consistent with the presence of the hydrogen bonds.

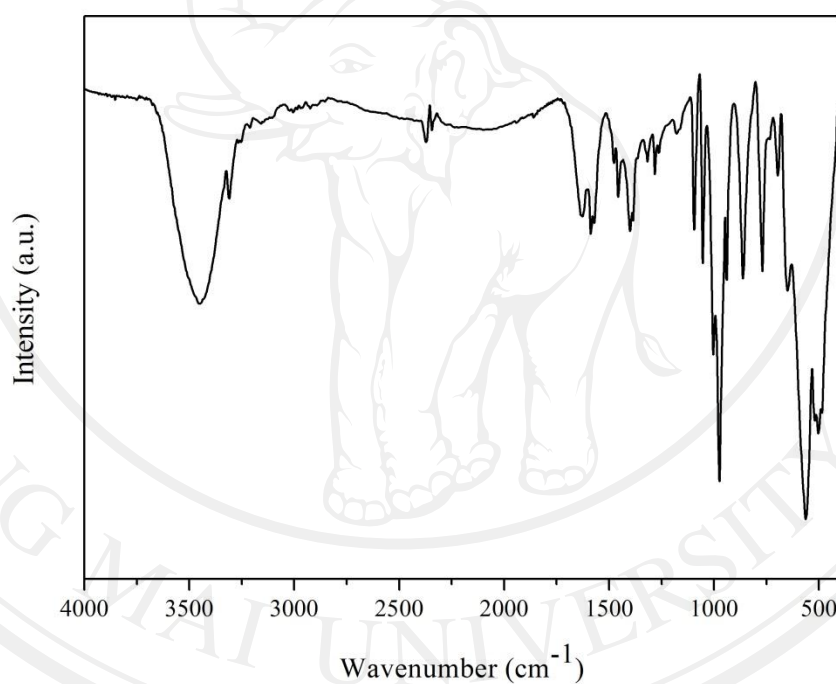


Figure 2.5 FT–IR spectrum collected on the ground crystals of compound I.

2.3 Conclusions

In conclusion, a new pillared POV layer structure of the Co–POV system has been prepared and fully characterized; $\text{Co}(\text{C}_2\text{N}_2\text{H}_8)_2[\text{V}_4^{\text{IV}}\text{V}_2^{\text{V}}\text{O}_{14}]$ (**I**). This expands a series of the pillared POV layer structures to include Zn–POV, Cu–POV, Ni–POV and Co–POV, which in turn suggest the template function of the en and therefore the feasibility in extending this structural series to other secondary metals with possibly better potential functions.

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