

CHAPTER II

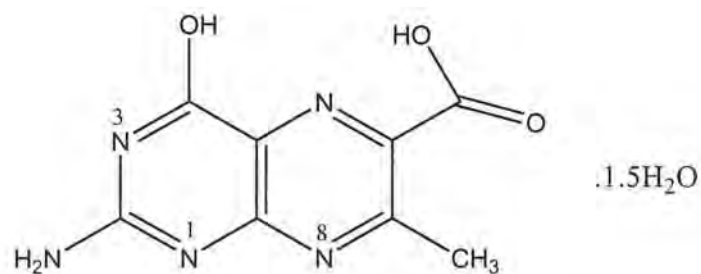
**Synthesis and x-ray structural characterization of a
Co(II) – complex of 2-amino-7-methyl-4-oxidopterin-
-6-carboxylic acid with 1,10-phenanthroline as the
ancillary ligand**

Abstract

In the relevant compound $[\text{Co}(\text{C}_8\text{H}_5\text{N}_5\text{O}_3)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})].3\text{H}_2\text{O}$ (**2**), a tridentate 2-amino-7-methyl-4-oxidopterin-6-carboxylate ligand (**1**), a bidentate ancillary 1,10-phenanthroline (phen) ligand and a water molecule complete a distorted octahedral geometry around the Co^{II} atom. The pterin ligand forms two chelate rings. The phen and pterin ring systems are nearly perpendicular [dihedral angle = $85.15(8)^\circ$]. $\text{N}-\text{H}\cdots\text{O}$, $\text{O}-\text{H}\cdots\text{N}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds link the complex molecules and lattice water molecules into a layer parallel to (001). π - π stacking contacts (involving phen-phen and pteridine-pteridine) are also observed [centroid-centroid distances = $3.670(2)$, $3.547(2)$, $3.698(2)$ and $3.349(2)$ Å].

Introduction

The primary motivation for pursuing coordination chemistry of pterins is the ubiquitous presence of this heterocyclic system in nature including a substantial number of metalloenzymes^{2,7,9,10}. Literature survey reveals the existence of only a few X-ray structurally characterized cobalt-pterin/pteridine/lumazine complexes as well as one containing an organocobalt moiety^{1,3,8,11}. The concerned ligands usually act as bidentate O,N-donors and none of the above complexes possesses a typical π -acceptor ancillary ligand like 1,10-phenanthroline (phen). In this case a typical tridentate ONO-donor pterin ligand [Scheme (II-1)] has been utilized for the present study. In this crystallographic study on the mixed ligand cobalt(II) complex as mentioned under title, possessing both a tridentate pterin ligand and a π -acidic ligand like phen, different



Scheme (II-1): Structural formula of the free pterin ligand (1) (H_2L^1)

aspects are considered, e.g. crystal, molecular and electronic structures.

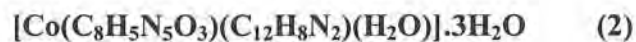
A CHEM3D model of this cobalt(II) complex (2) has also been obtained through MM2 calculations⁴⁴. Few selected bond lengths and angles obtained by this method have been compared with the corresponding X-ray data¹¹⁷, for exploring the reliability of the CHEM3D models as applied for the present coordination compounds of the different pterin ligands, delineated in this thesis⁴⁴.

Experimental

Materials

2-amino-7-methyl-4-oxidopteridine-6-carboxylic acid sesquihydrate ($C_8H_7N_5O_3 \cdot 1.5H_2O$) (1) was obtained by published procedure¹⁸. 1,10-phenanthroline monohydrate has been obtained from E. Merck.

Synthesis



The title complex (2) was prepared by the dropwise addition of an

aqueous alkaline solution (NaOH: 11 mg, 0.275 mmol) of the pterin ligand (**1**) (31 mg, 0.125 mmol) to a warm (311 K) aqueous reaction medium containing $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (35 mg, 0.125 mmol) and 1,10-phenanthroline monohydrate (25 mg, 0.125 mmol) in a total volume of 60 ml. The pH value was adjusted to 10.8 using aqueous NaOH solution and dioxygen was bubbled in for 48 h; final pH was 10.3. Initially a small amount of yellow-white precipitate came out and the reaction mixture ultimately assumed a reddish-pink tinge. It was transferred to a 100 ml beaker, requisite quantity of water was added to make up for the evaporation loss and allowed to stand at room temperature. Pink crystals suitable for single-crystal diffraction appeared after 15 days (yield: 30%).

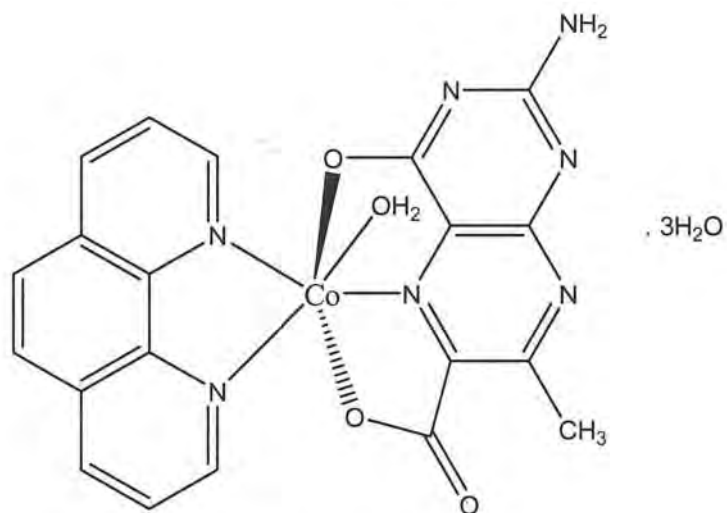
X – ray structural Investigation

Data collection

APEX2 (Bruker, 2007); cell refinement: SAINT ⁶; data reduction: SAINT; program(s) used to solve structure: SHELXS97 ¹⁶; program(s) used to refine structure: CRYSTALS ⁵; molecular graphics: CAMERON ¹⁷; software used to prepare material for publication: CRYSTALS.

Refinement

The H-atoms were all located in a difference map, but those attached to C atoms were repositioned geometrically. The H atoms were initially refined with soft restrains on the bond lengths and angles to regularize their geometry (C-H = 0.93-0.98, N-H = 0.86-0.89, O-H = 0.82 Å) and with $U_{\text{iso}}(\text{H}) = 1.2-1.5U_{\text{eq}}(\text{parent atom})$, after which the positions were refined with rigiding constrains.



Scheme (II-2)

Crystal data

$[\text{Co}(\text{C}_8\text{H}_5\text{N}_5\text{O}_3)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})], 3\text{H}_2\text{O}$

$M_r = 530.36$

Triclinic, $P\bar{1}$

$a = 8.454 (2) \text{ \AA}$

$b = 9.934 (3) \text{ \AA}$

$c = 13.778 (4) \text{ \AA}$

$\alpha = 97.534 (4)^\circ$

$\beta = 95.281 (4)^\circ$

$\gamma = 110.603 (4)^\circ$

$V = 1061.8 (5) \text{ \AA}^3$

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 0.87 \text{ mm}^{-1}$

$T = 110 \text{ K}$

$0.23 \times 0.11 \times 0.04 \text{ mm}$

Data collection

Bruker Kappa APEXII CCD

diffractometer

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

8945 measured reflections

4726 independent reflections

4360 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$$T_{\min} = 0.82, T_{\max} = 0.97$$

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.057$$

$$wR(F^2) = 0.129$$

$$S = 1.03$$

4726 reflection

316 parameters

H-atom parameters constrained

$$\Delta\rho_{\max} = 0.99 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.88 \text{ e } \text{\AA}^{-3}$$

Table (II-1): Hydrogen-bond geometry (\AA , $^\circ$).

D-H...A	D-H	H...A	D...A	D-H...A
N7-H141...O2 ⁱ	0.85	2.12	2.942 (4)	163
N7-H142...O6 ⁱⁱ	0.84	2.15	2.970 (4)	165
O4-H181...O6	0.81	1.93	2.717 (3)	164
O4-H182...N5 ⁱⁱ	0.80	2.25	3.051 (4)	176
O5-H341...O1	0.82	2.34	3.079 (4)	151
O5-H341...O2	0.82	2.23	2.896 (4)	139
O5-H342...N4 ⁱⁱⁱ	0.82	2.04	2.844 (4)	166
O6-H351...O5	0.83	1.92	2.740 (4)	174
O6-H352...N5 ^{iv}	0.82	2.05	2.871 (4)	176
O7-H331...O5 ⁱ	0.80	2.25	2.941 (4)	145
O7-H332...O3	0.81	2.23	2.962 (5)	151

Symmetry codes: (i) $x + 1, y + 1, z$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x - 1, y - 1, z$; (iv) $x, y - 1, z$.

Results and Discussion

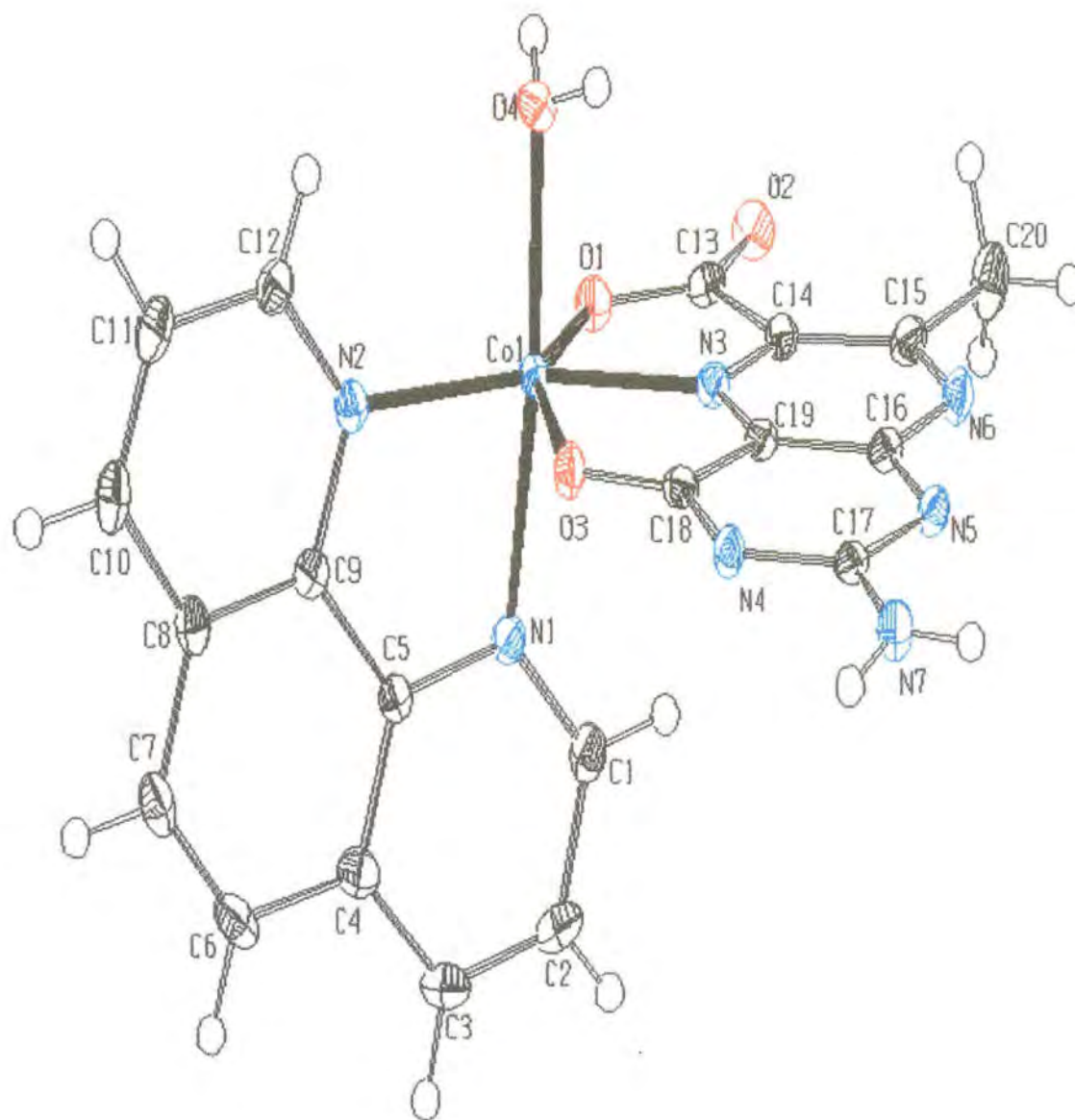


Fig.(II-1): The molecular structure of the title compound $[\text{Co}(\text{C}_8\text{H}_5\text{N}_5\text{O}_3)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ (**2**). Displacement ellipsoids are drawn at the 50% probability level. Lattice water molecules are omitted for clarity.

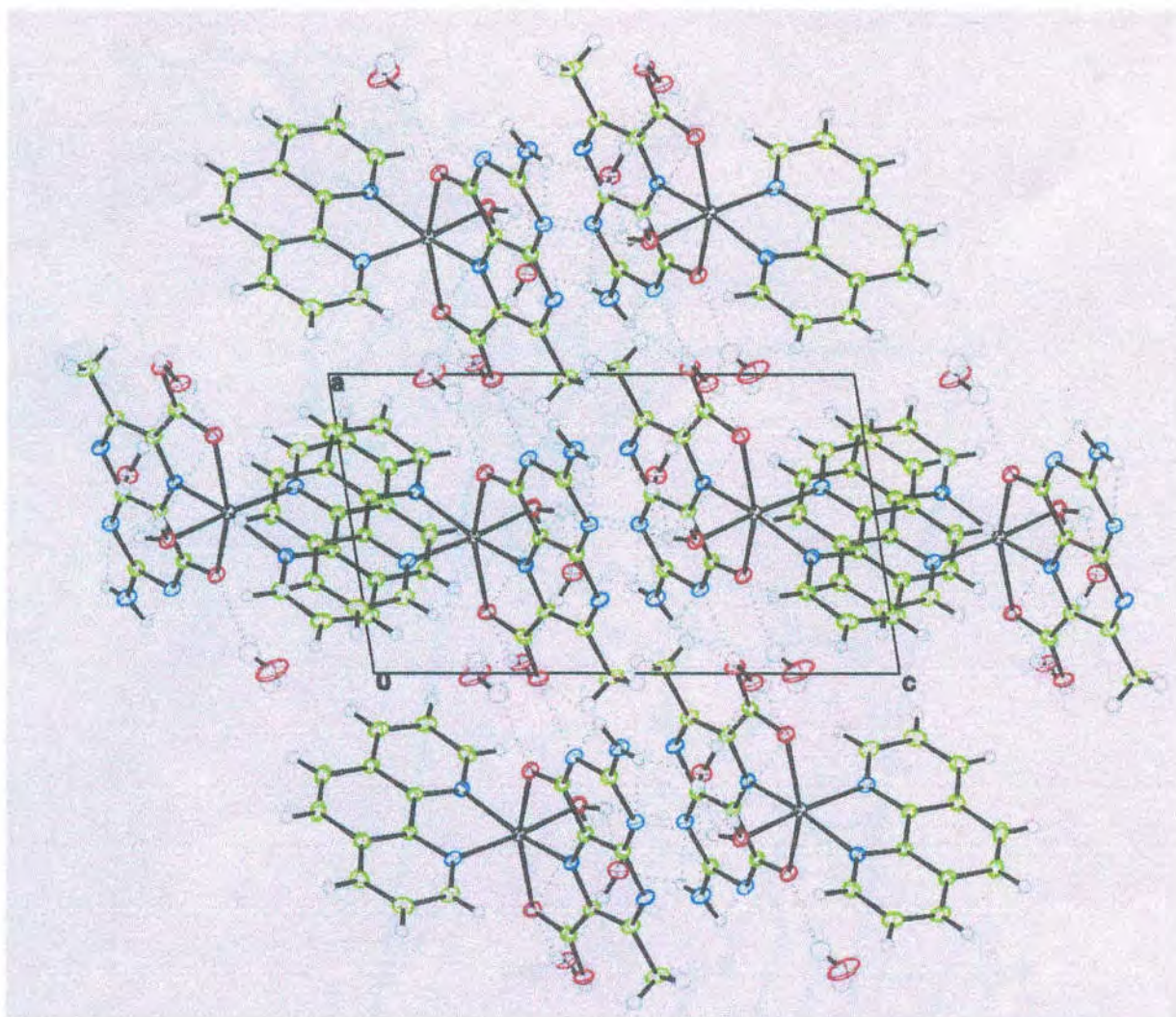


Fig.(II-2): The crystal packing diagram of the title compound, viewed along the b axis. Dotted lines indicate hydrogen bonds, assisting the formation of a layer structure parallel to (001).

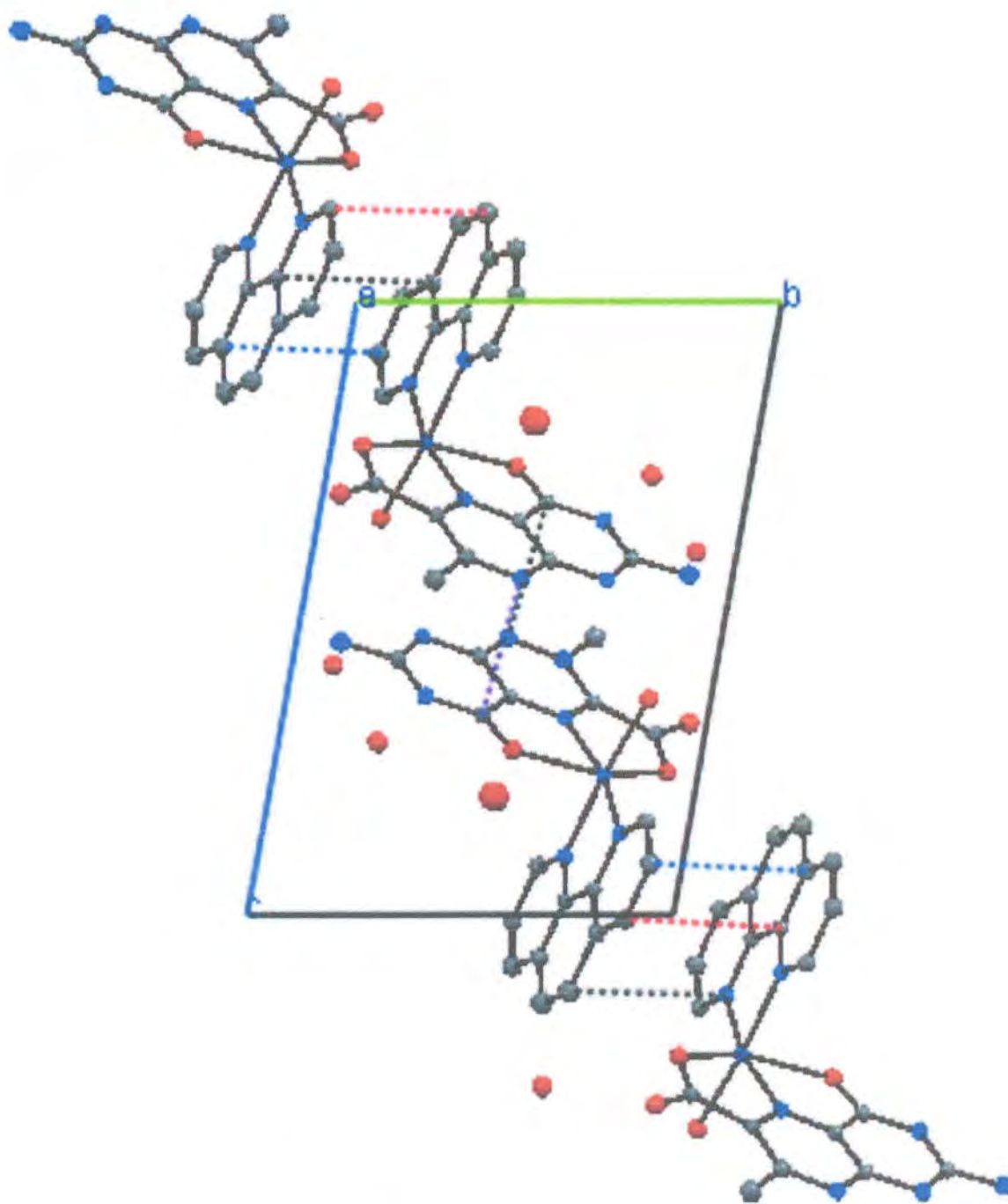


Fig.(II-3): A molecular packing diagram highlighting π - π stacking interactions between two neighbouring phen-phen and pterin-pterin rings, respectively.

Table (II-2): Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.45982 (5)	0.22172 (4)	0.22887 (3)	0.0125
O1	0.2062 (3)	0.0747 (2)	0.23341 (17)	0.0176
C13	0.1224 (4)	0.1182 (3)	0.2948 (2)	0.0159
O2	-0.0205 (3)	0.0408 (2)	0.31159 (18)	0.0204
C14	0.2096 (4)	0.2762 (3)	0.3463 (2)	0.0150
N3	0.3618 (3)	0.3367 (3)	0.32052 (19)	0.0137
C19	0.4572 (4)	0.4746 (3)	0.3559 (2)	0.0137
C16	0.4012 (4)	0.5628 (3)	0.4205 (2)	0.0151
N5	0.4986 (3)	0.7057 (3)	0.4529 (2)	0.0154
C17	0.6493 (4)	0.7539 (3)	0.4170 (2)	0.0157
N4	0.7169 (3)	0.6739 (3)	0.3559 (2)	0.0161
C18	0.6243 (4)	0.5321 (3)	0.3254 (2)	0.0148
O3	0.6704 (3)	0.4463 (2)	0.26886 (17)	0.0174
N7	0.7460 (4)	0.8957 (3)	0.4440 (2)	0.0199
H141	0.8293	0.9343	0.4135	0.0223*
H142	0.7086	0.9522	0.4775	0.0228*
N6	0.2466 (3)	0.5028 (3)	0.4504 (2)	0.0176
C15	0.1508 (4)	0.3621 (3)	0.4146 (2)	0.0171
C20	-0.0163 (4)	0.2992 (4)	0.4506 (3)	0.0256
H172	-0.0359	0.3696	0.4963	0.0378*
H173	-0.0185	0.2188	0.4829	0.0383*

H171	-0.1061	0.2680	0.3985	0.0380*
O4	0.5538 (3)	0.1469 (2)	0.35063 (17)	0.0185
H181	0.4964	0.0663	0.3597	0.0272*
H182	0.5418	0.1894	0.4013	0.0271*
N2	0.3758 (3)	0.2801 (3)	0.0963 (2)	0.0162
C12	0.2567 (4)	0.3370 (4)	0.0798 (3)	0.0196
C11	0.2191 (4)	0.3750 (4)	-0.0116 (3)	0.0230
C10	0.3071 (4)	0.3548 (4)	-0.0867 (3)	0.0220
C8	0.4354 (4)	0.2958 (4)	-0.0719 (2)	0.0183
C9	0.4634 (4)	0.2593 (3)	0.0218 (2)	0.0138
C5	0.5897 (4)	0.1963 (3)	0.0422 (2)	0.0147
N1	0.6075 (3)	0.1592 (3)	0.1330 (2)	0.0152
C1	0.7247 (4)	0.1018 (3)	0.1537 (2)	0.0178
C2	0.8260 (4)	0.0749 (4)	0.0839 (3)	0.0225
C3	0.8069 (4)	0.1096 (4)	-0.0079 (3)	0.0221
C4	0.6854 (4)	0.1721 (3)	-0.0323 (2)	0.0179
C6	0.6545 (4)	0.2115 (4)	-0.1271 (3)	0.0227
C7	0.5346 (5)	0.2690 (4)	-0.1461 (3)	0.0241
H321	0.5124	0.2898	-0.2083	0.0280*
H311	0.7136	0.1926	-0.1771	0.0268*
H291	0.8704	0.0898	-0.0554	0.0258*
H281	0.9086	0.0377	0.1020	0.0257*
H271	0.7401	0.0814	0.2171	0.0208*
H221	0.2815	0.3779	-0.1477	0.0263*

H211	0.1346	0.4115	-0.0211	0.0270*
H201	0.1976	0.3531	0.1304	0.0229*
O7	0.9931 (4)	0.4695 (3)	0.1919 (3)	0.0445
H331	1.0355	0.5568	0.1993	0.0644*
H332	0.9309	0.4819	0.2305	0.0648*
O5	0.0341 (3)	-0.2327 (3)	0.28207 (18)	0.0224
H341	0.0418	-0.1559	0.2637	0.0322*
H342	-0.0472	-0.2571	0.3124	0.0321*
O6	0.3374 (3)	-0.0951 (2)	0.40693 (18)	0.0204
H351	0.2468	-0.1420	0.3696	0.0287*
H352	0.3795	-0.1552	0.4182	0.0294*

Table (II-3): Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0135 (2)	0.0131 (2)	0.0129 (2)	0.00622 (16)	0.00458 (15)	0.00324 (15)
O1	0.0164 (11)	0.0142 (11)	0.0210 (12)	0.0040 (9)	0.0048 (9)	0.0026 (9)
C13	0.0156 (15)	0.0157 (15)	0.0168 (15)	0.0064 (12)	-0.0002 (12)	0.0050 (12)
O2	0.0143 (11)	0.0173 (11)	0.0269 (13)	0.0015 (9)	0.0059 (9)	0.0056 (10)
C14	0.0134 (14)	0.0150 (15)	0.0185 (15)	0.0062 (12)	0.0048 (12)	0.0053 (12)
N3	0.0134 (12)	0.0130 (12)	0.0153 (13)	0.0049 (10)	0.0035 (10)	0.0038 (10)
C19	0.0139 (14)	0.0141 (14)	0.0156 (15)	0.0062 (12)	0.0053 (12)	0.0057 (12)
C16	0.0158 (15)	0.0172 (15)	0.0152 (15)	0.0085 (12)	0.0029 (12)	0.0050 (12)
N5	0.0149 (13)	0.0129 (12)	0.0196 (14)	0.0060 (10)	0.0040 (10)	0.0030 (10)
C17	0.0157 (15)	0.0175 (15)	0.0167 (15)	0.0083 (12)	0.0030 (12)	0.0063 (12)
N4	0.0150 (13)	0.0148 (13)	0.0202 (14)	0.0057 (10)	0.0078 (11)	0.0047 (11)

C18	0.0144 (15)	0.0169 (15)	0.0150 (15)	0.0065 (12)	0.0036 (12)	0.0063 (12)
O3	0.0173 (11)	0.0170 (11)	0.0193 (12)	0.0073 (9)	0.0065 (9)	0.0028 (9)
N7	0.0188 (14)	0.0136 (13)	0.0264 (15)	0.0044 (11)	0.0081 (12)	0.0020 (11)
N6	0.0164 (13)	0.0169 (13)	0.0224 (14)	0.0083 (11)	0.0071 (11)	0.0041 (11)
C15	0.0148 (15)	0.0171 (15)	0.0226 (16)	0.0075 (12)	0.0065 (12)	0.0079 (13)
C20	0.0163 (16)	0.0207 (17)	0.040 (2)	0.0056 (14)	0.0126 (15)	0.0024 (15)
O4	0.0198 (12)	0.0193 (11)	0.0174 (11)	0.0069 (9)	0.0052 (9)	0.0063 (9)
N2	0.0151 (13)	0.0150 (13)	0.0203 (14)	0.0061 (10)	0.0063 (11)	0.0055 (11)
C12	0.0169 (16)	0.0171 (15)	0.0263 (18)	0.0064 (13)	0.0075 (13)	0.0055 (13)
C11	0.0193 (17)	0.0195 (16)	0.0319 (19)	0.0082 (14)	0.0003 (14)	0.0098 (14)
C10	0.0202 (17)	0.0232 (17)	0.0224 (17)	0.0061 (14)	-0.0007 (13)	0.0107 (14)
C8	0.0177 (16)	0.0168 (15)	0.0178 (16)	0.0030 (12)	0.0007 (12)	0.0044 (13)
C9	0.0133 (14)	0.0114 (14)	0.0153 (15)	0.0026 (11)	0.0032 (11)	0.0022 (11)
C5	0.0129 (14)	0.0113 (14)	0.0176 (15)	0.0020 (11)	0.0022 (12)	0.0015 (12)
N1	0.0152 (13)	0.0133 (12)	0.0158 (13)	0.0040 (10)	0.0034 (10)	0.0013 (10)
C1	0.0171 (15)	0.0150 (15)	0.0199 (16)	0.0058 (12)	0.0002 (12)	0.0005 (12)
C2	0.0169 (16)	0.0214 (17)	0.0312 (19)	0.0103 (14)	0.0035 (14)	0.0025 (14)
C3	0.0162 (16)	0.0190 (16)	0.0298 (19)	0.0059 (13)	0.0079 (14)	-0.0016 (14)
C4	0.0152 (15)	0.0162 (15)	0.0200 (16)	0.0032 (12)	0.0055 (13)	0.0009 (13)
C6	0.0241 (17)	0.0251 (17)	0.0181 (17)	0.0072 (14)	0.0093 (14)	0.0026 (14)
C7	0.0299 (19)	0.0254 (18)	0.0169 (16)	0.0070 (15)	0.0085 (14)	0.0086 (14)
O7	0.0352 (16)	0.0272 (15)	0.074 (2)	0.0127 (13)	0.0292 (16)	-0.0010 (15)
O5	0.0178 (11)	0.0184 (12)	0.0318 (14)	0.0057 (9)	0.0095 (10)	0.0059 (10)
O6	0.0192 (12)	0.0166 (11)	0.0266 (13)	0.0077 (9)	0.0020 (10)	0.0060 (10)

Table (II-4): Geometric parameters (Å, °)

Co1-O1	2.140 (2)	N2-C12	1.333 (4)
Co1-N3	2.016 (3)	N2-C9	1.355 (4)
Co1-O3	2.270 (2)	C12-C11	1.402 (5)
Co1-O4	2.120 (2)	C12-H201	0.923
Co1-N2	2.123 (3)	C11-C10	1.363 (5)
Co1-N1	2.079 (3)	C11-H211	0.914
O1-C13	1.279 (4)	C10-C8	1.414 (5)
C13-O2	1.244 (4)	C10-H221	0.926
C13-C14	1.519 (4)	C8-C9	1.408 (4)
C14-N3	1.319 (4)	C8-C7	1.435 (5)
C14-C15	1.426 (4)	C9-C5	1.439 (4)
N3-C19	1.319 (4)	C5-N1	1.359 (4)
C19-C16	1.397 (4)	C5-C4	1.411 (4)
C19-C18	1.450 (4)	N1-C1	1.333 (4)
C16-N5	1.354 (4)	C1-C2	1.406 (5)
C16-N6	1.360 (4)	C1-H271	0.930
N5-C17	1.360 (4)	C2-C3	1.363 (5)
C17-N4	1.378 (4)	C2-H281	0.928
C17-N7	1.337 (4)	C3-C4	1.412 (5)
N4-C18	1.335 (4)	C3-H291	0.928
C18-O3	1.265 (4)	C4-C6	1.439 (5)
N7-H141	0.852	C6-C7	1.349 (5)
N7-H142	0.843	C6-H311	0.925

N6-C15	1.342 (4)	C7-H321	0.926
C15-C20	1.491 (4)	O7-H331	0.800
C20-H172	0.947	O7-H332	0.810
C20-H173	0.960	O5-H341	0.811
C20-H171	0.930	O5-H342	0.820
O4-H181	0.810	O6-H351	0.830
O4-H182	0.801	O6-H352	0.820
O1-Co1-N3	75.10 (10)	H172-C20-H171	106.6
O1-Co1-O3	151.22 (8)	H173-C20-H171	109.7
N3-Co1-O3	76.26 (9)	Co1-O4-H181	116.6
O1-Co1-O4	90.13 (9)	Co1-O4-H182	109.7
N3-Co1-O4	90.23 (10)	H181-O4-H182	95.0
O3-Co1-O4	92.74 (9)	Co1-N2-C12	128.8 (2)
O1-Co1-N2	90.99 (10)	Co1-N2-C9	112.7 (2)
N3-Co1-N2	96.45 (10)	C12-N2-C9	118.5 (3)
O3-Co1-N2	89.46 (9)	N2-C12-C11	122.3 (3)
O4-Co1-N2	173.29 (10)	N2-C12-H201	119.1
O1-Co1-N1	119.55 (10)	C11-C12-H201	118.6
N3-Co1-N1	164.48 (10)	C12-C11-C10	119.6 (3)
O3-Co1-N1	88.76 (9)	C12-C11-H211	120.2
O4-Co1-N1	94.58 (10)	C10-C11-H211	120.2
N2-Co1-N1	79.12 (10)	C11-C10-C8	119.9 (3)
Co1-O1-C13	116.8 (2)	C11-C10-H221	120.1

O1-C13 -O2	124.1 (3)	C8 - C10 - H221	120.0
O1-C13 -C14	114.6 (3)	C10 - C8 - C9	116.7 (3)
O2 - C13 - C14	121.2 (3)	C10 - C8 - C7	124.4 (3)
C13 - C14 - N3	111.4 (3)	C9 - C8 - C7	118.9 (3)
C13 - C14 - C15	129.9 (3)	C8 - C9 - N2	123.1 (3)
N3 - C14 - C15	118.8 (3)	C8 - C9 - C5	120.1 (3)
Co1-N3 -C14	121.6 (2)	N2 - C9 - C5	116.8 (3)
Co1-N3 -C19	117.6 (2)	C9 - C5 - N1	117.5 (3)
C14 - N3 - C19	120.8 (3)	C9 - C5 - C4	119.5 (3)
N3 - C19 - C16	121.8 (3)	N1 - C5 - C4	123.0 (3)
N3 - C19 - C18	117.4 (3)	Co1 - N1 - C5	113.6 (2)
C16 - C19 - C18	120.7 (3)	Co1 - N1 - C1	127.6 (2)
C19 - C16 - N5	120.8 (3)	C5 - N1 - C1	118.5 (3)
C19 - C16 - N6	118.7 (3)	N1 - C1 - C2	122.0 (3)
N5 - C16 - N6	120.4 (3)	N1 - C1 - H271	118.0
C16 - N5 - C17	115.1 (3)	C2 - C1 - H271	120.0
N5 - C17 - N4	127.9 (3)	C1 - C2 - C3	119.8 (3)
N5 - C17 - N7	117.0 (3)	C1 - C2 - H281	119.3
N4 - C17 - N7	115.1 (3)	C3 - C2 - H281	120.9
C17 - N4 - C18	117.6 (3)	C2 - C3 - C4	119.9 (3)
C19 - C18 - N4	117.7 (3)	C2 - C3 - H291	120.7
C19 - C18 - O3	118.1 (3)	C4 - C3 - H291	119.4
N4 - C18 - O3	124.2 (3)	C3 - C4 - C5	116.8 (3)
Co1 - O3 - C18	110.63 (19)	C3 - C4 - C6	124.2 (3)

C17 - N7 - H141	119.8	C5 - C4 - C6	119.0 (3)
C17 - N7 - H142	119.9	C4 - C6 - C7	121.2 (3)
H141 - N7 - H142	117.6	C4 - C6 - H311	119.5
C16 - N6 - C15	119.0 (3)	C7 - C6 - H311	119.2
C14 - C15 - N6	120.8 (3)	C8 - C7 - C6	121.3 (3)
C14 - C15 - C20	121.7 (3)	C8 - C7 - H321	118.4
N6 - C15 - C20	117.4 (3)	C6 - C7 - H321	120.3
C15 - C20 - H172	111.5	H331 - O7 - H332	86.2
C15 - C20 - H173	110.1	H341 - O5 - H342	108.7
H172 - C20 - H173	108.2	H351 - O6 - H352	105.5
C15 - C20 - H171	110.7		

In the title compound (**2**) [Figure (II-1)], the stereochemistry around the Co^{II} atom is essentially distorted octahedral with two N atoms of phen, a pyrazine ring N atom (N3) of the pterin ligand and an aqua O atom forming the equatorial plane; two pterin O atoms (O1 and O3) define the longer axial positions, with the phenolate O3 forming the longest axial bond [2.270 (2) Å]. Extent of distortion of this coordination octahedron is much more pronounced as compared to that of the Co(II)-pteridine complexes reported earlier^{1,8,11}. A major cause of this departure from regular geometry is that the pterin ligand forms two five-membered chelate rings having small bite angles [75.10 (10) and 76.29 (9)°], instead of only one per pteridine ligand for the earlier cases. Location of the short Co1 - N3 bond [2.016 (3) Å] in the equatorial plane is consistent with the literature, which suggests a strong cobalt-pterin interaction¹³. The pterin ligand is coordinated here as a binategative tridentate ONO donor, as evident from the charge

balance of this complex. The phen and pterin rings are nearly perpendicular to each other for minimizing the steric repulsion. The Co1-N1 [2.079 (3) Å] and Co1-N2 [2.123 (3) Å] bond lengths are at par with that of the Co1-N3 bond [2.016 (3) Å] and indicate receipt of π -back donation to both phen and pterin rings from the Co(II) centre (d^7) through $d\pi$ - $p\pi$ interactions. This process is further strengthened by the presence of π -donating phenolate and carboxylate O atoms around the metal centre¹².

For rationalizing the near double bond nature of the O3-C18 [1.265 (4) Å] bond, a hypothesis of Joule^{4,14} may be invoked, which suggests withdrawal of electron density from the pyrazine ring N6 by the pyrimidine ring C18-carbonyl group through mesomeric interaction. Formation of the O3-Co1 bond accentuates this electron withdrawal towards O3. The electron-rich N7-C17 [1.337 (4) Å] bond may also participate in this electron transfer. The pyrimidine ring is fairly planar and deviations of the C16/N5/C17 and C17/N4/C18 segments with respect to the N7-C17 multiple bonds are 2.6 and 0.7°, respectively.

In the crystal, intermolecular N-H \cdots O, O-H \cdots N and O-H \cdots O hydrogen bonds [Table (II-1)] link the complex molecules and lattice water molecules into a layer parallel to (001) [Figure (II-2)]. The lattice water molecules are decisive for the crystal packing. Figure (II-3) reveals π - π stacking interactions involving two parallel, inversion-related pterin rings within the same unit cell and showing face-to-face distance of 3.283 (4) and 3.366 (4) Å. Again the phen rings display two types of π - π stacking on either side of the unit cell. In one case, the adjacent phen rings are essentially parallel to each other with an average interplanar distance of 3.496 (4) Å; on the other side of

the unit cell, the face-to-face separations between parallel phen rings are 3.578 (4) and 3.629 (5) Å.

Comparison of X-ray structural data of (2) with those obtained from MM2 calculations for its CHEM3D model

Table (II-5) shows a comparison of selected bond length data (Å) of complex (2) obtained X-ray structurally [Figure (II-1); Table (II-4)] with the corresponding data of the CHEM3D model of this complex [Figure (II-4)]^{44,117}. For this purpose, the

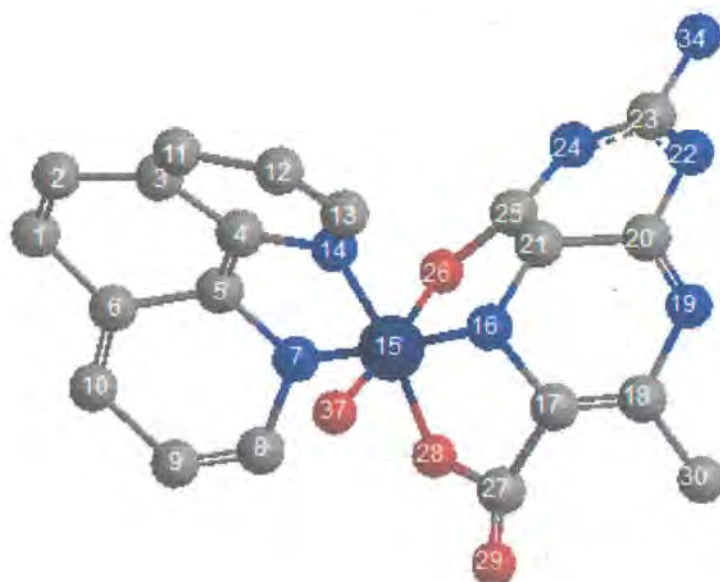


Fig.(II-4): The optimized geometry (CHEM3D model obtained through MM2 calculations) of $[\text{Co}(\text{C}_8\text{H}_5\text{N}_3\text{O}_3)(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})].3\text{H}_2\text{O}$ (2) with a steric energy of 39.4 kcal mol⁻¹. Its numbering system is set by the software used⁴⁴ and is different from that in Fig.(II-1).

numbering system of the ORTEP diagram [Figure (II-1)] has been followed here, with the corresponding numbering system of the CHEM3D model being shown side by side. Table (II-6) shows a similar comparison of a few selected bond angles (deg) data.

Table (II-5): Comparison of selected single crystal X-ray bond lengths of (2) with the corresponding CHEM3D bond lengths.

Bond length of atoms			
X-ray / ORTEP [Fig.(II-1)]		CHEM3D [Fig.(II-4)]	
Co(1) – N(2)	2.123(3)	Co(15) – N(7)	1.872
Co(1) – N(1)	2.079(3)	Co(15) – N(14)	1.875
Co(1) – O(3)	2.270(2)	Co(15) – O(26)	1.836
Co(1) – N(3)	2.016(3)	Co(15) – N(16)	1.862
Co(1) – O(1)	2.140(2)	Co(15) – O(28)	1.837
Co(1) – O(4)	2.120(2)	Co(15) – O(37)	1.821

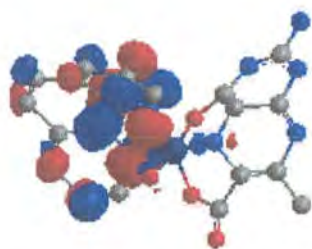
Table (II-6): Comparison of selected single crystal X-ray bond angles of (2) with the corresponding CHEM3D bond angles

Bond angle atoms			
X-ray / ORTEP [Fig.(II-1)]		CHEM3D [Fig.(II-4)]	
N(2) – Co(1) – N(1)	79.12(10)	N(7) – Co(15) – N(14)	87.02
N(1) – Co(1) – O(3)	88.76(9)	N(14) – Co(15) – O(26)	85.40
O(3) – Co(1) – N(3)	76.26(9)	O(26) – Co(15) – N(16)	86.99
N(3) – Co(1) – O(1)	75.10(10)	N(16) – Co(15) – O(28)	92.87
O(1) – Co(1) – O(4)	90.13(9)	O(28) – Co(15) – O(37)	85.17
O(4) – Co(1) – N(2)	94.58(10)	O(37) – Co(15) – N(7)	92.11

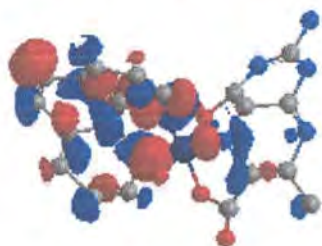
Reasonable correspondence between the two sets of the above data establish reliability of the CHEM3D models (MM2 calculations) as applied in this thesis⁴⁴.

Electronic structures on the basis of CHEM3D models (MM2 calculations)

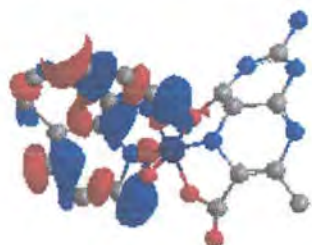
The CHEM3D models have been utilized for visualizing the frontier



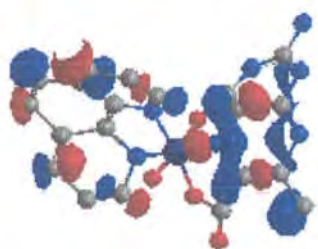
$$E_4(\text{LUMO}+1) = -8.15 \text{ eV} \quad (2)$$



$$E_3(\text{LUMO}) = -8.25 \text{ eV}$$



$$E_2(\text{HOMO}) = -8.77 \text{ eV}$$



$$E_1(\text{HOMO}-1) = -9.15 \text{ eV}$$

$$\Delta(E_2-E_1) = 0.38 \text{ eV}$$

$$\Delta(E_3-E_2) = 0.52 \text{ eV}$$

$$\Delta(E_4-E_3) = 0.10 \text{ eV}$$

Fig.(II-5): The visualized frontier orbitals with energies (E, eV) of (2) (using Chem Office 2004, version 8.0).

orbitals with energies (eV) of the pertinent complexes, throughout the thesis ⁴⁴. Such electronic structures have proved valuable in rationalizing the reactivity data of these complexes.

The visualized frontier orbitals of (2) are presented in Figure (II-5) as an example ⁴⁴.

Conclusion

This chapter highlights the synthesis of a new Co(II) – pterin complex (2), its crystallization and X-ray structure determination. As stated at the outset, only few such data are available till date. The X-ray data throw light not only on the molecular structure of this complex, its hydrogen bonding and π - π stacking but also on the electron – shuffling ability of the pterin ligand residue. The latter aspect justifies the natural selection of pterins for a large number of metal containing biomolecules.

Finally, a comparison of the X-ray structural data of this complex with the corresponding CHEM3D data (MM2 calculations), shows the efficacy of the CHEM3D models as adopted in this thesis.