Supporting Information

For

Metal Tetraphosphonate “Wires” and Their Corrosion Inhibiting Passive Films

By

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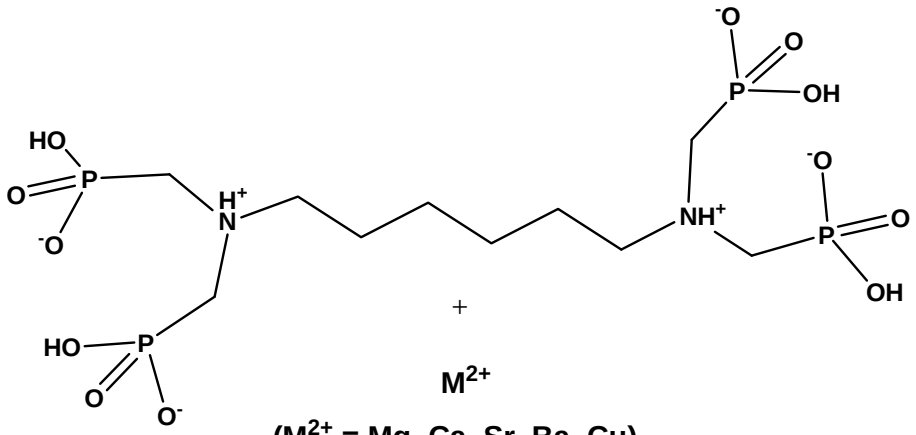
Contents

1. Syntheses Reaction Scheme



M^{2+}

(M^{2+} = Mg, Ca, Sr, Ba, Cu)

$(m+n)H_2O$

$\{[M(HO_3PCH_2)_2N(H)(CH_2)_6N(H)(CH_2PO_3H)_2(mH_2O)]\cdot nH_2O\} + 2H^+$

M = Mg (m = 0, n = 0)
$\{[Mg_2(HO_3PCH_2)_2N(H)(CH_2)_6N(H)(CH_2PO_3H)_2]$

M = Ca, m = 0, n = 2)
$\{[M(HO_3PCH_2)_2N(H)(CH_2)_6N(H)(CH_2PO_3H)_2]\cdot 2H_2O\}$

M = Sr (m = 6, n = 2)
$\{[Sr(HO_3PCH_2)_2N(H)(CH_2)_6N(H)(CH_2PO_3H)_2(6H_2O)]\cdot 2H_2O\}$

M = Ba (m = 6, n = 2)
$\{[Ba(HO_3PCH_2)_2N(H)(CH_2)_6N(H)(CH_2PO_3H)_2(6H_2O)]\cdot 2H_2O\}$

M = Cu (m = 4, n = 6)
$\{[Cu(HO_3PCH_2)_2N(H)(CH_2)_6N(H)(CH_2PO_3H)_2(4H_2O)]\cdot 6H_2O\}$

Figure S-1.1. Syntheses Reaction Scheme

2. Elemental analyses

For 1 (Sr-HDTMP)
Calculated for $C_{10}H_{42}N_2O_{20}P_4Sr$ ([Sr(HDTMP)$(H_2O)_6$]·$2H_2O$, MW 721.96):
Calcd. C, 16.62; H, 5.82; N, 3.88
Found C, 16.68; H, 5.85; N, 3.85

For 2 (Ba-HDTMP)
Calculated for $C_{10}H_{42}BaN_2O_{20}P_4$ ([Ba(HDTMP)$(H_2O)_6$]·$2H_2O$, MW 771.68):
Calcd. C, 15.56; H, 5.44; N, 3.63
Found C, 16.87; H, 5.11; N, 3.87

For 3 (Cu-HDTMP) (No satisfactory elemental analysis was possible for this compound, because of the presence of multi-phase products)
Calculated for $C_{10}H_{46}CuN_2O_{22}P_4$ ([Cu(HDTMP)$(H_2O)_4$]·$6H_2O$] MW 733.91):
Calcd. C, 16.35; H, 6.27; N, 3.82
Found C, 20.81; H, 4.86; N, 4.81
Found C, 22.65; H, 5.54; N, 5.58

For 1a (Sr2-HDTMP, synthesis at pH = 7)
Calculated for $C_{10}H_{48}N_2O_{24}P_4Sr_2$ ([Sr_2(HDTMP)$(H_2O)_{12}$], MW 875.24):
Calcd. C, 13.71; H, 5.48; N, 3.20
Found C, 12.87; H, 4.63; N, 3.11

For 2a (Ba2-HDTMP, synthesis at pH = 7)
Calculated for $C_{10}H_{48}N_2O_{24}P_4Ba_2$ ([Ba_2(HDTMP)$(H_2O)_{12}$], MW 974.66):
Calcd. C, 12.31; H, 4.92; N, 2.87
Found C, 12.38; H, 4.70; N, 3.07

For Mg-HDTMP
Calculated for $C_{10}H_{26}N_2O_{12}P_4Mg_2$ ([Mg_2(HDTMP)], MW 538.82):
Calcd. C, 22.29; H, 4.86; N, 5.19
Found C, 22.05; H, 5.06; N, 5.34
Absence of water of crystallization was confirmed by thermodiffraction. Mg-HDTMP exhibits a stable XRD pattern up to 250 ºC). Further temperature increase leads to $Mg_2P_4O_{12}$ (pdf # 01-070-1803) as the only identifiable crystalline comppound (see below in “XRD Powder Patterns”).

For Ca-HDTMP
Calculated for $C_{10}H_{30}N_2O_{14}P_4Ca$ ([Ca(HDTMP)]·$2H_2O$, MW 566.32):
Calcd. C, 21.21; H, 5.34; N, 4.95
Found C, 20.92; H, 4.98; N, 5.16

3. XRD Powder Patterns

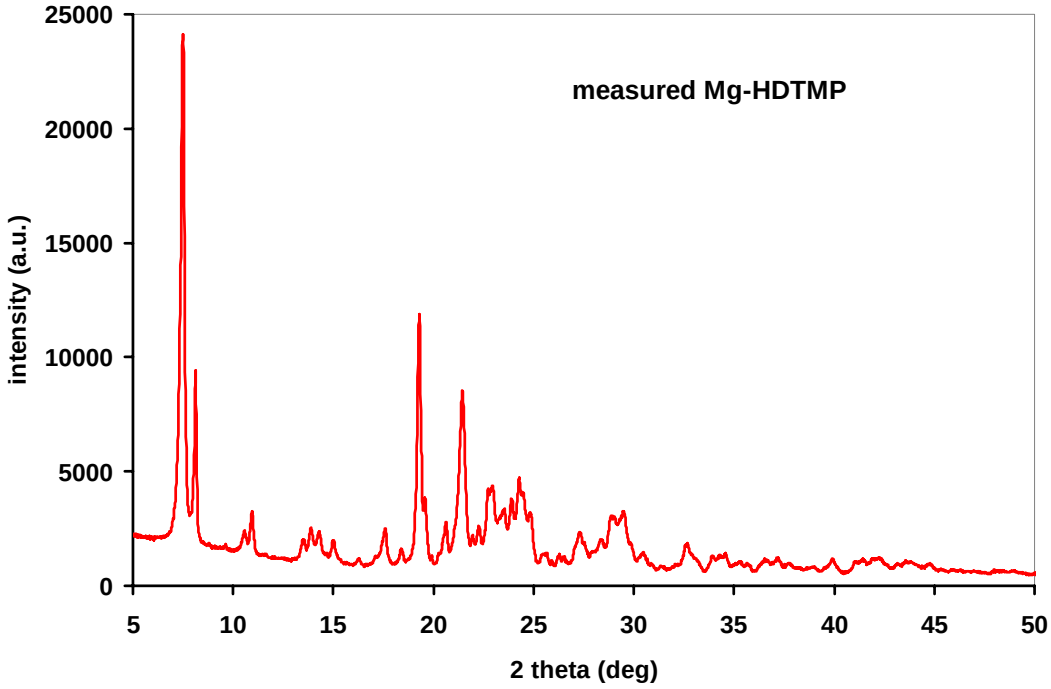


Figure S-3.1. Measured XRD powder pattern for Mg-HDTMP

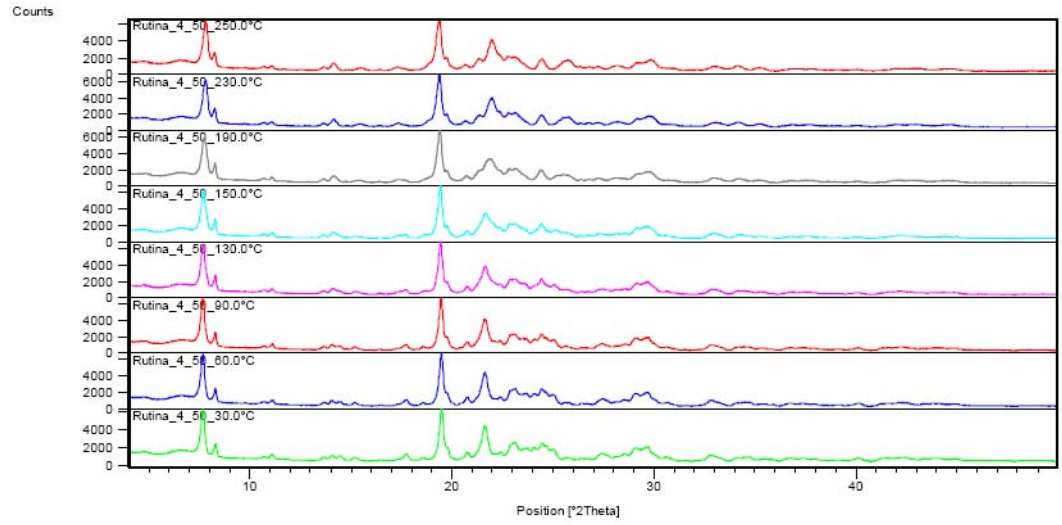


Figure S-3.2. Thermodiffraction study for Mg-HDTMP, proving that it is an anhydrous compound that is stable up to 250 ^{o}C.

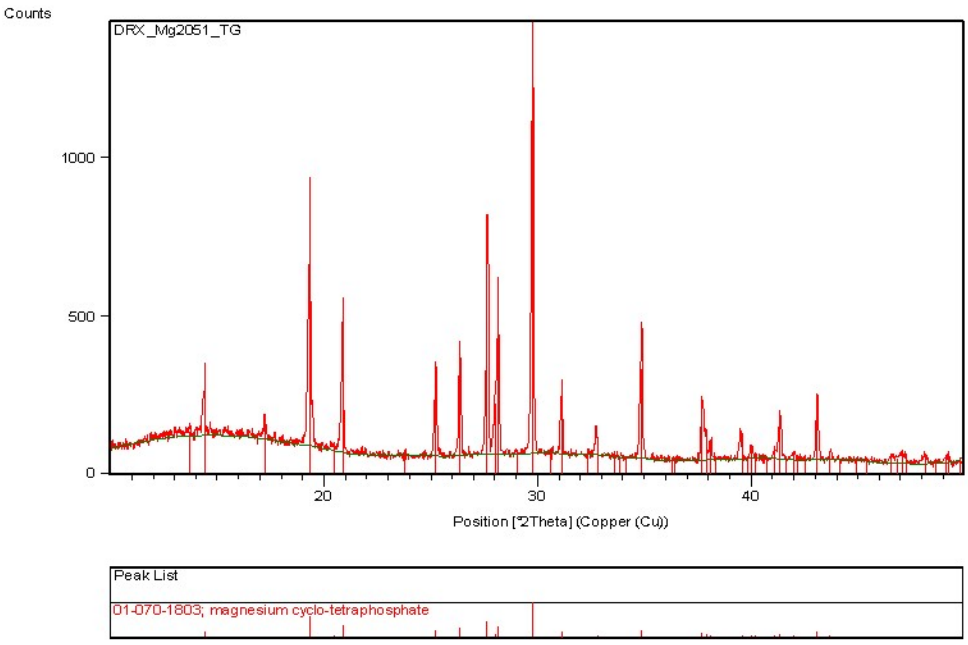


Figure S-3.3. The only crystalline product after decomposition of Mg-HDTMP is $Mg_2P_4O_{12}$ (pdf # 01-070-1803).

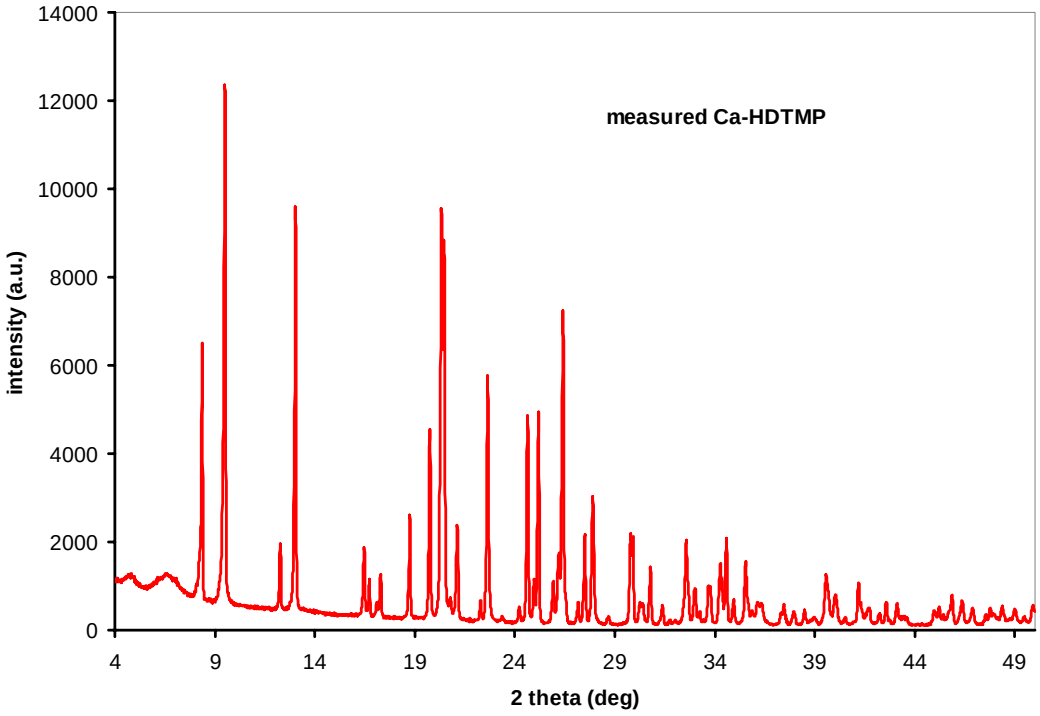


Figure S-3.4. Measured XRD powder pattern for Ca-HDTMP

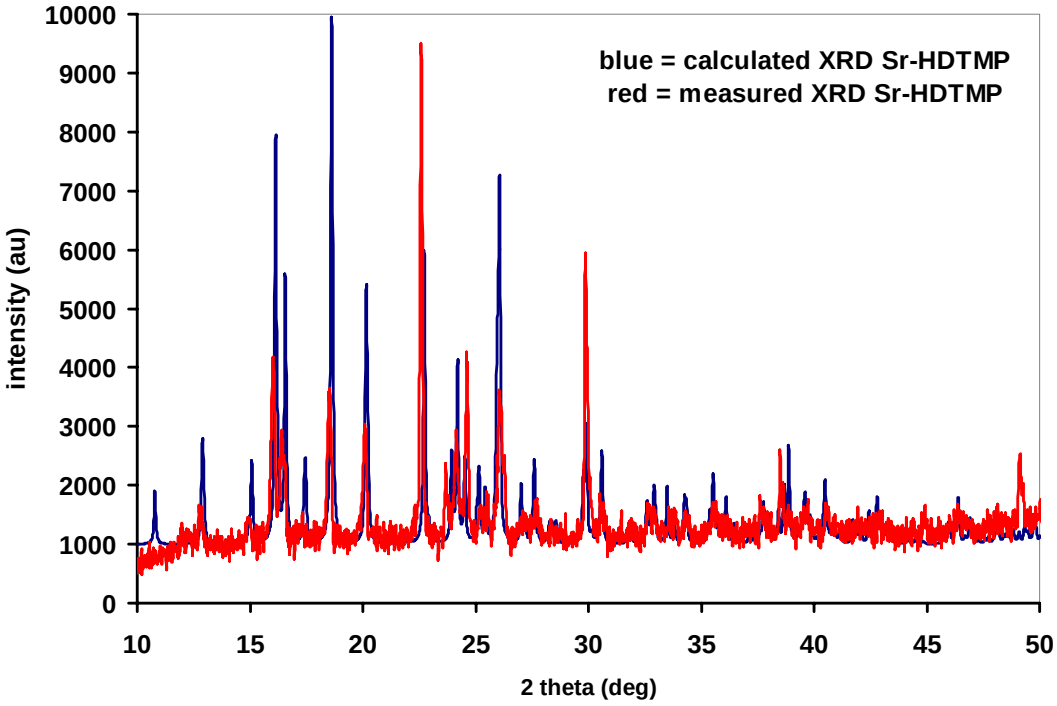


Figure S-3.5. Measured and theoretical XRD powder patterns for Sr-HDTMP

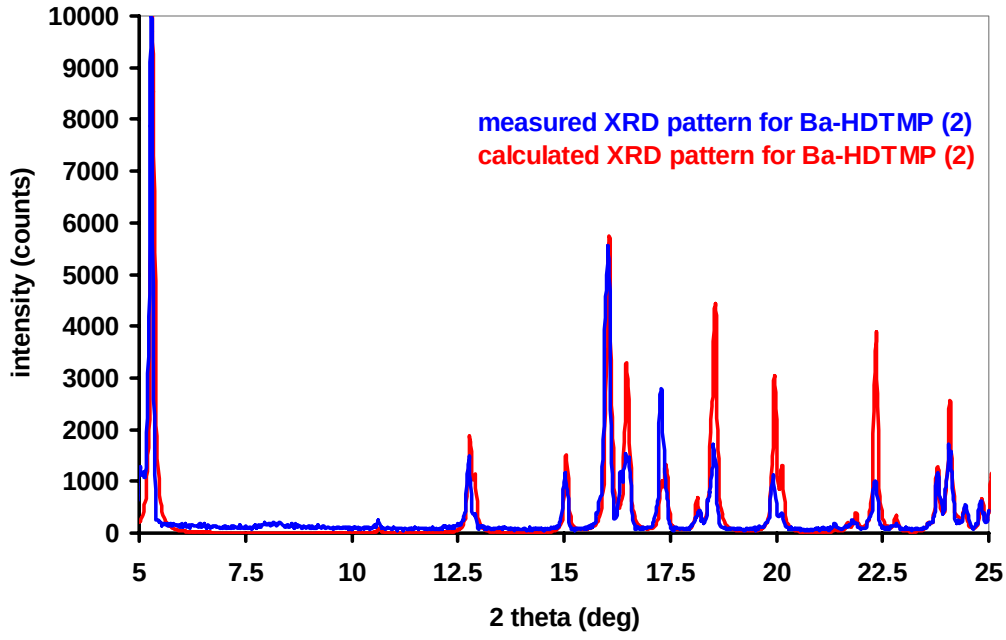


Figure S-3.6. Measured and theoretical XRD powder patterns for Ba-HDTMP

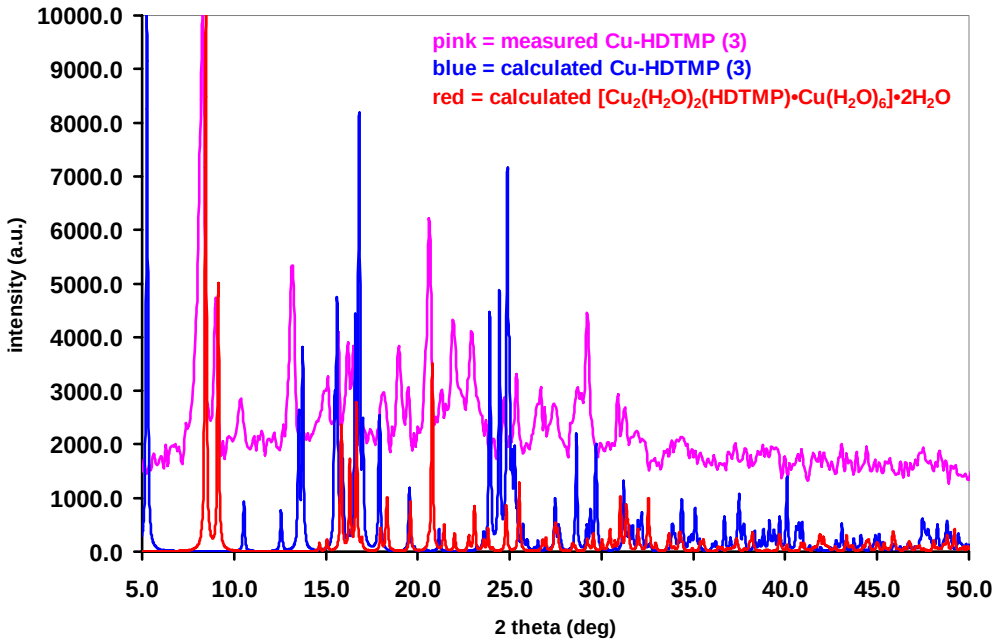


Figure S-3.7. Measured and theoretical XRD powder patterns for Cu-HDTMP

(It was impossible to isolate a single-phase Cu-HDTMP compound. The difference between calculated and measured XRD is obvious)

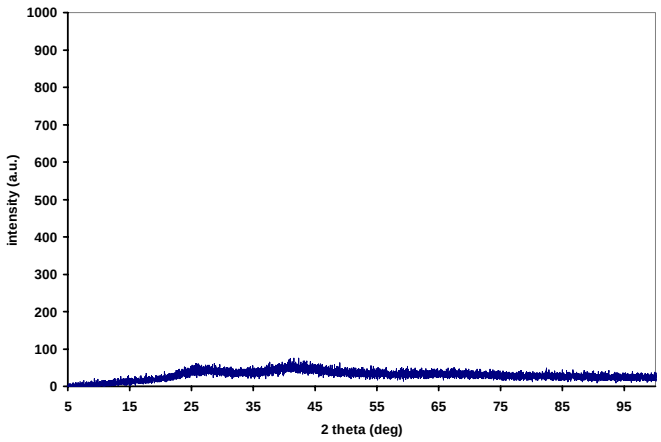


Figure S-3.8. Measured XRD powder pattern for the film formed in the presence of Sr+HDTMP at pH 7.0. The material is amorphous.

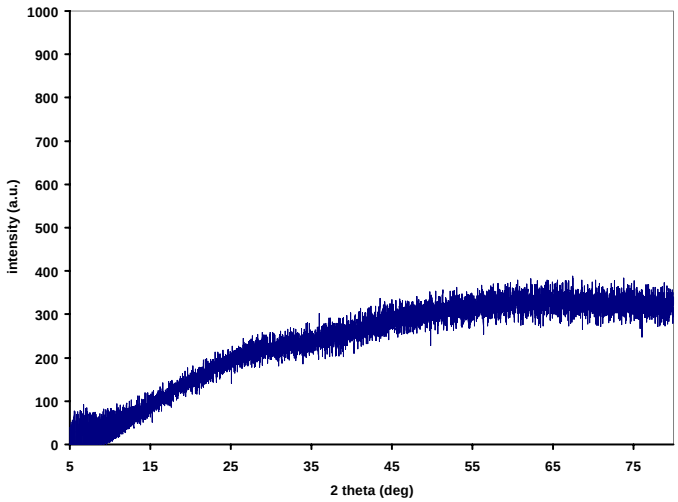


Figure S-3.9. Measured XRD powder pattern for the film formed in the presence of Ba+HDTMP at pH 7.0. The material is amorphous.

4. TGA Results

Ca-HDTMP

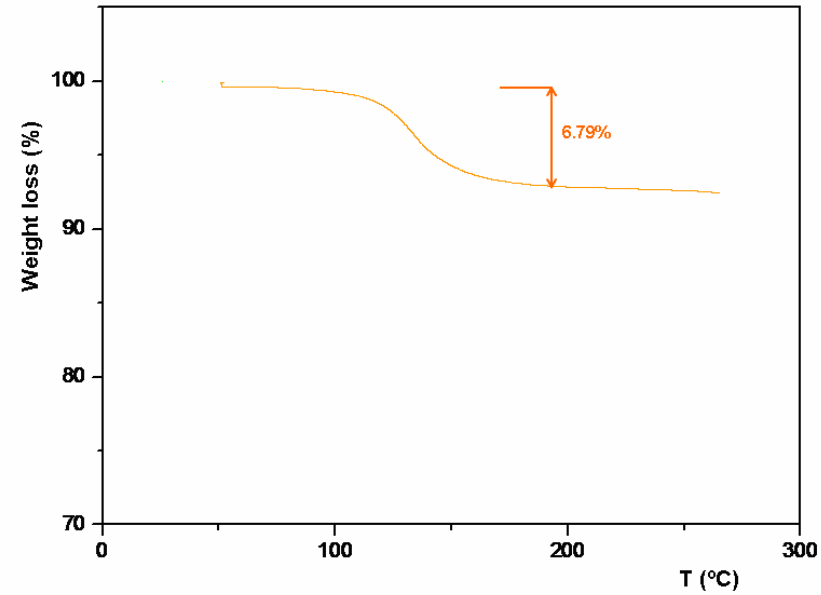


Figure S-4.1. TGA study for Ca-HDTMP. Calculated mass loss for 2 water molecules is 6.35% (at ~ 250 °C), compared to the observed 6.79% by TGA analysis.

Ba-HDTMP

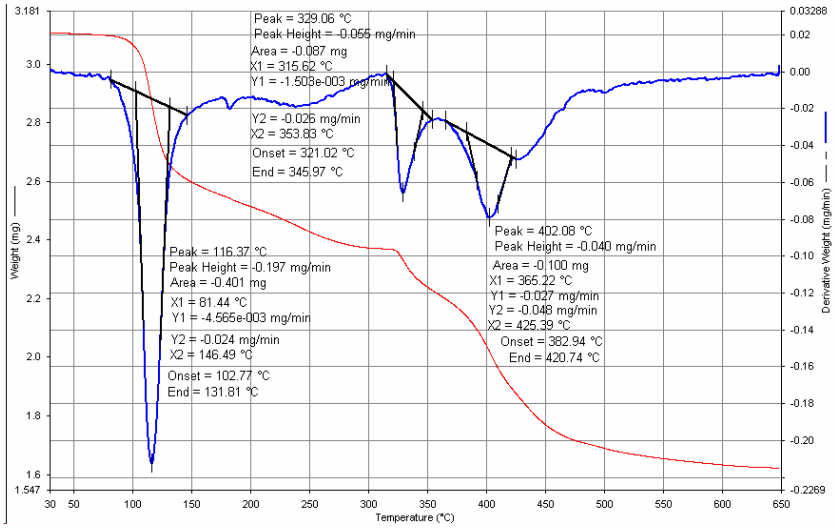


Figure S-4.2. TGA study for Ba-HDTMP. The peak at 116 °C represents a loss of 0.401 mg (12.85%), the one at 329 °C, 0.087 mg (2.8%), and the one at 402 °C, 0.100 mg (3.2%). Total measured loss 18.85 %. Calculated for 8 H_2O 18.67 %

Sr-HDTMP

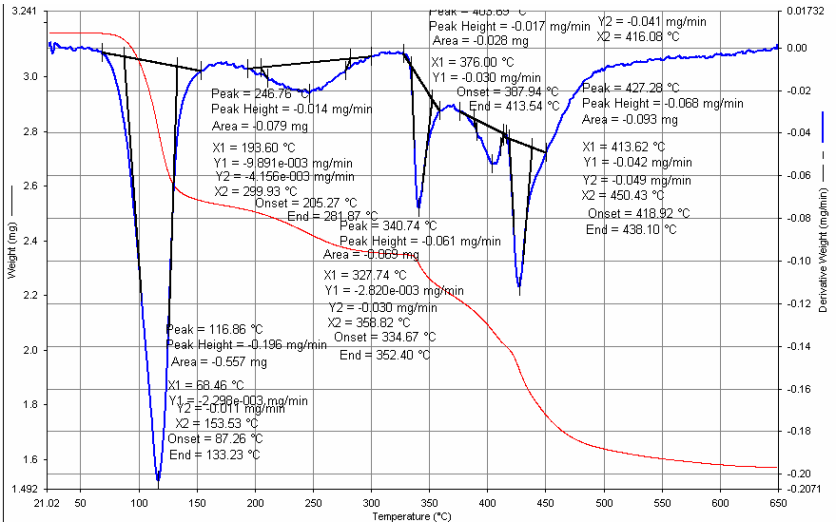


Figure S-4.3. TGA study for Sr-HDTMP. Total loss 20.87 % (calculated 19.94 %) for 8 H_2O molecules.

5. FT-IR Spectroscopy

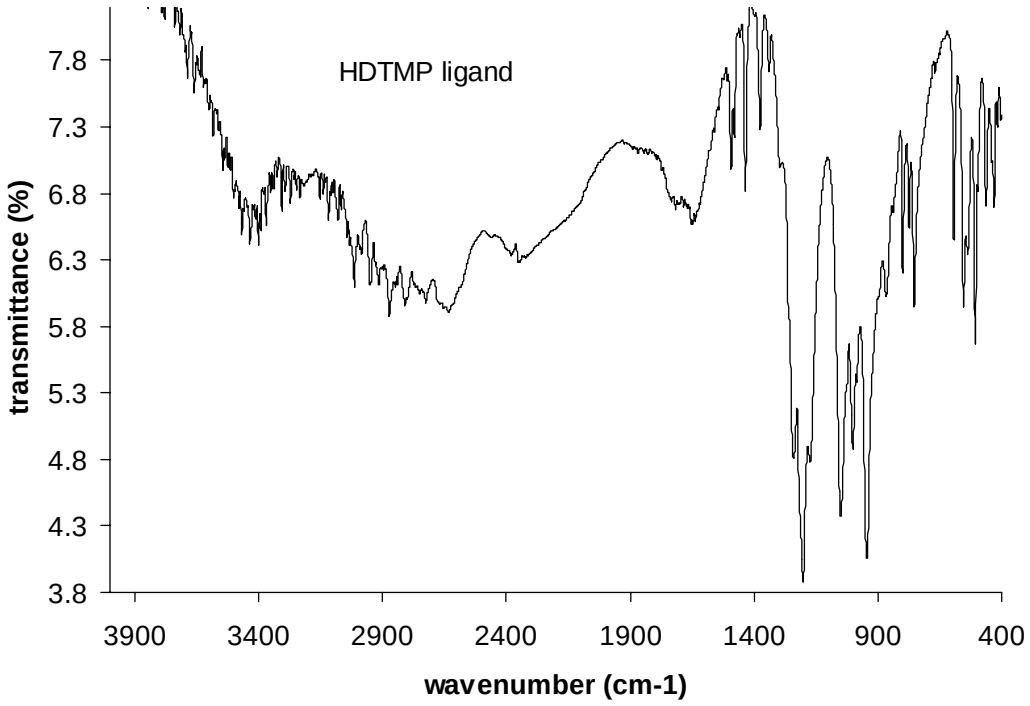


Figure S-5.1. FT-IR (in KBr pellets) of free HDTMP ligand.

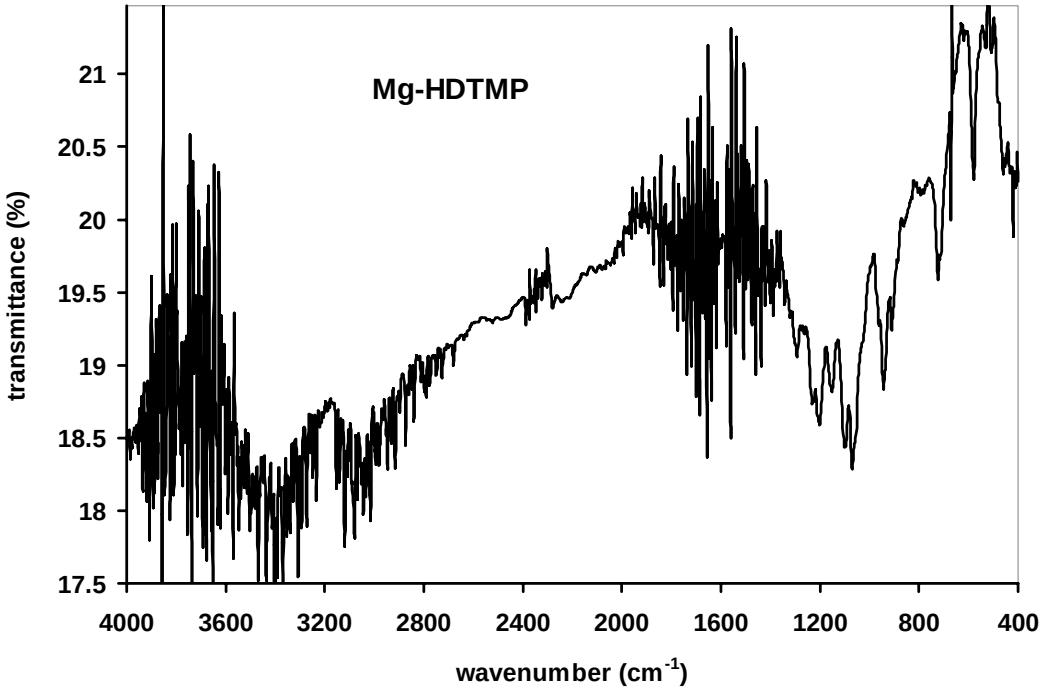


Figure S-5.2. FT-IR (in KBr pellets) of Mg-HDTMP (from synthesis at pH = 2).

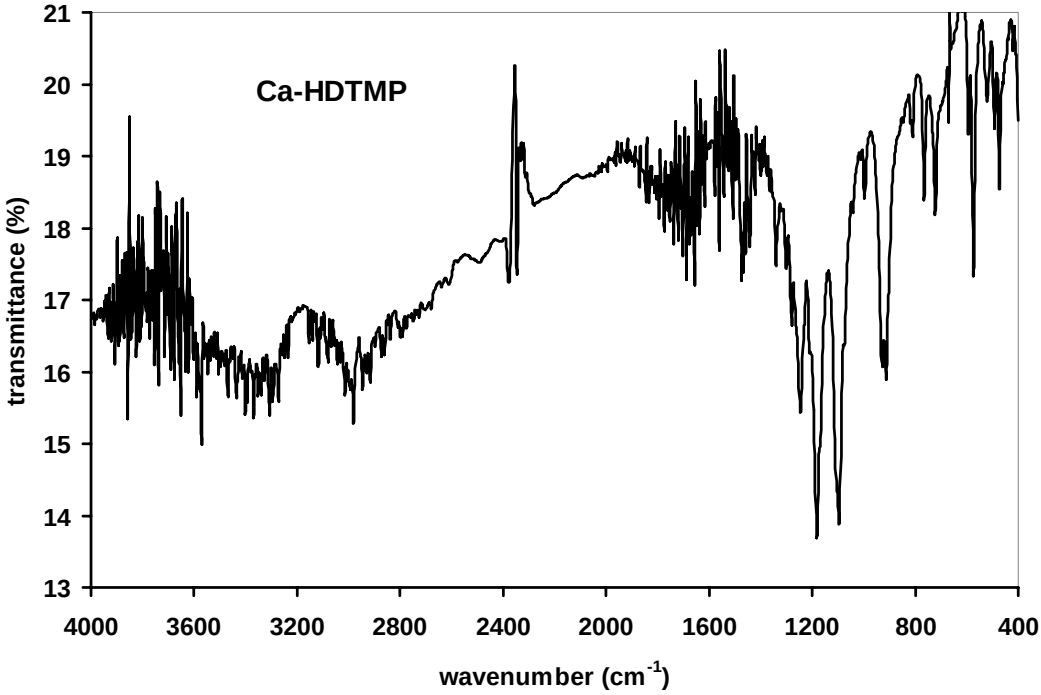


Figure S-5.3. FT-IR (in KBr pellets) of Ca-HDTMP (from synthesis at pH = 2).

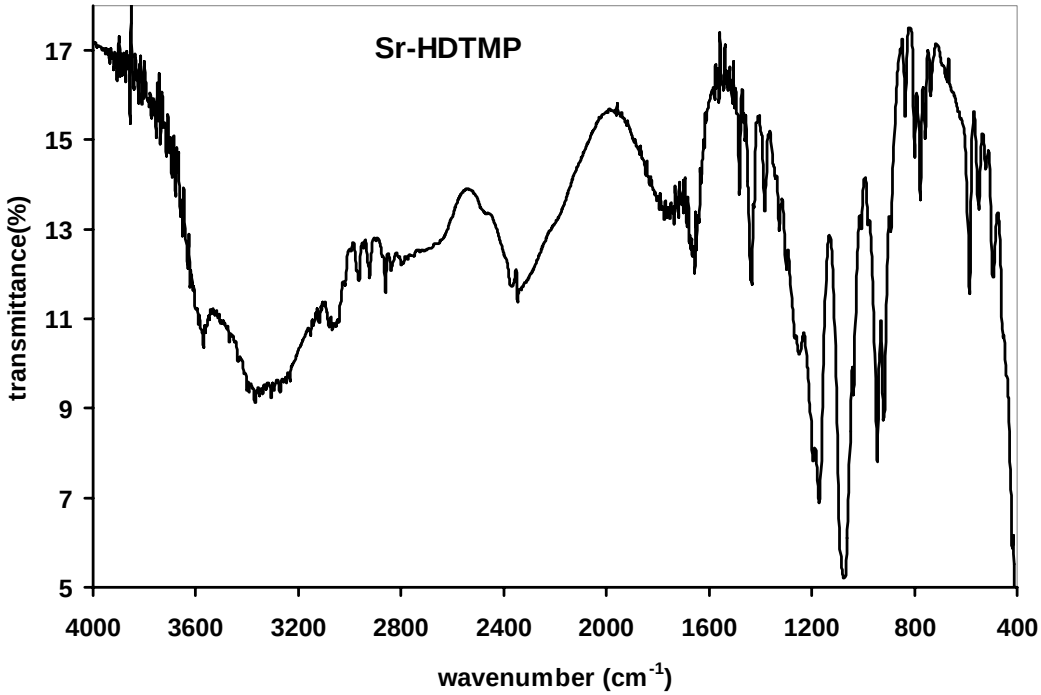


Figure S-5.4. FT-IR (in KBr pellets) of Sr-HDTMP (from synthesis at pH = 2).

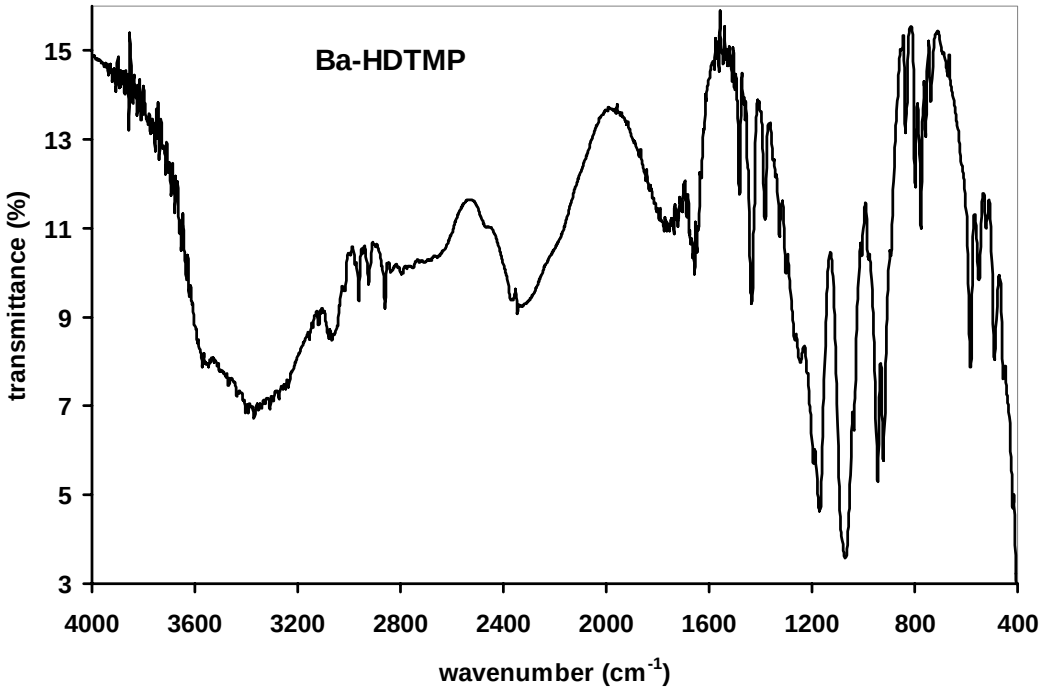


Figure S-5.6. FT-IR (in KBr pellets) of Ba-HDTMP (from synthesis at pH = 2).

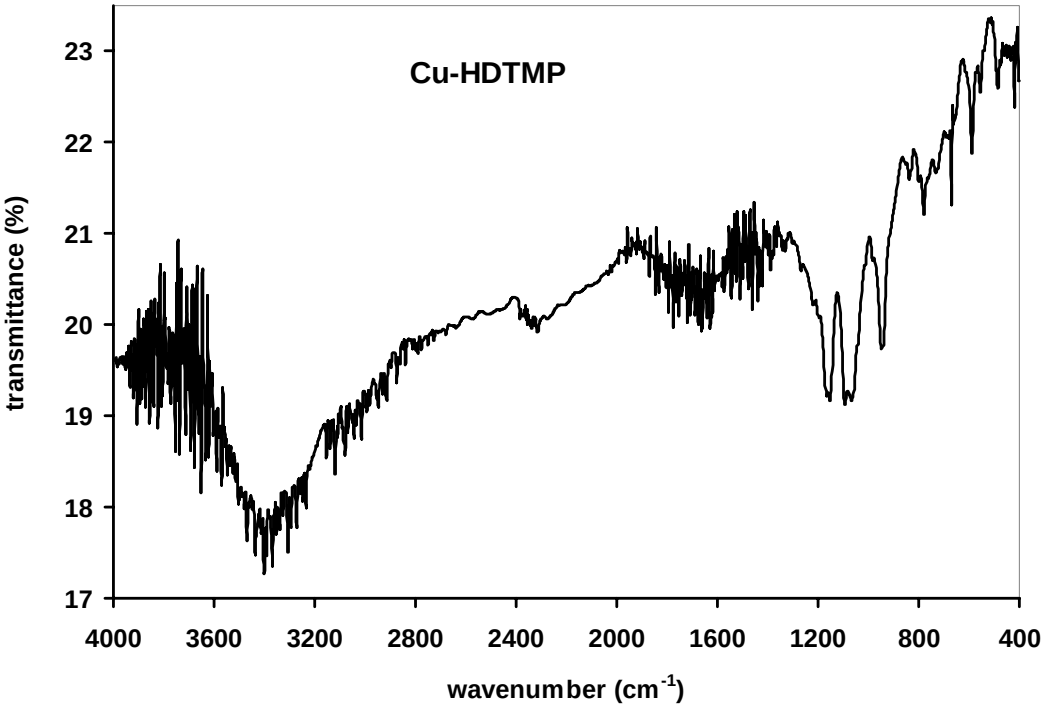


Figure S-5.7. FT-IR (in KBr pellets) of Cu-HDTMP (3) (from synthesis at pH = 2).

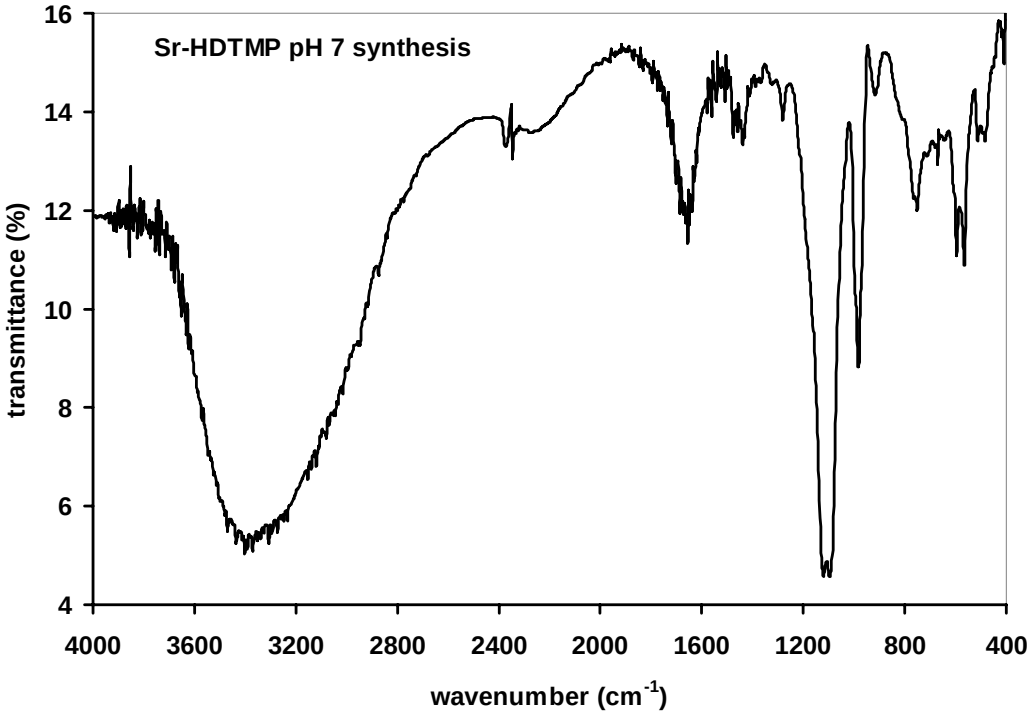


Figure S-5.8. FT-IR (in KBr pellets) of Sr-HDTMP (from synthesis at pH = 7).

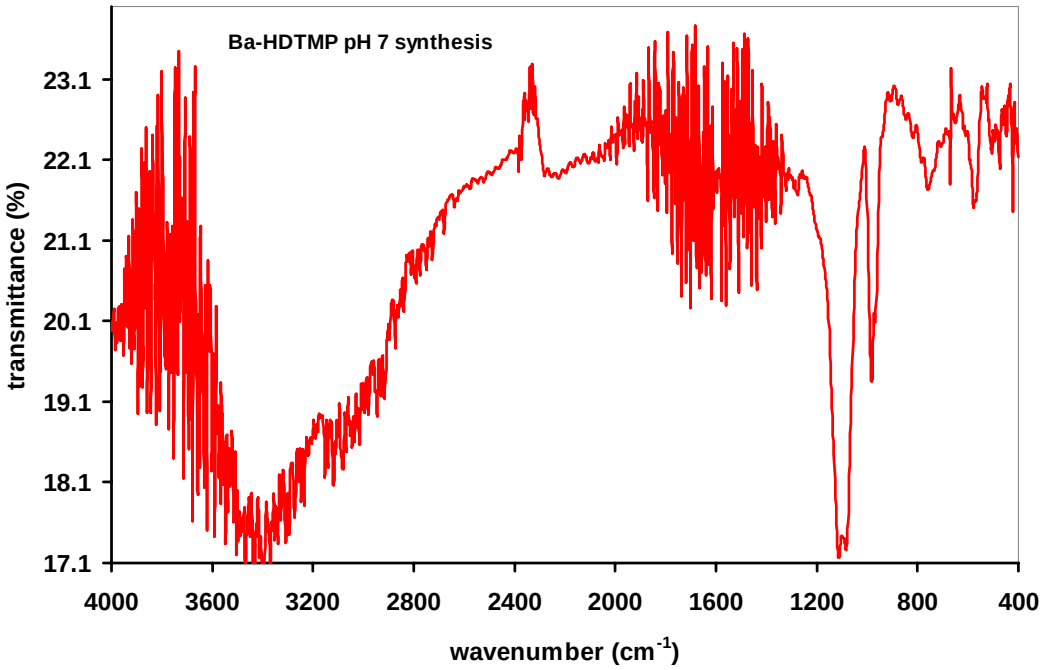


Figure S-5.9. FT-IR (in KBr pellets) of Ba-HDTMP (from synthesis at pH = 7).

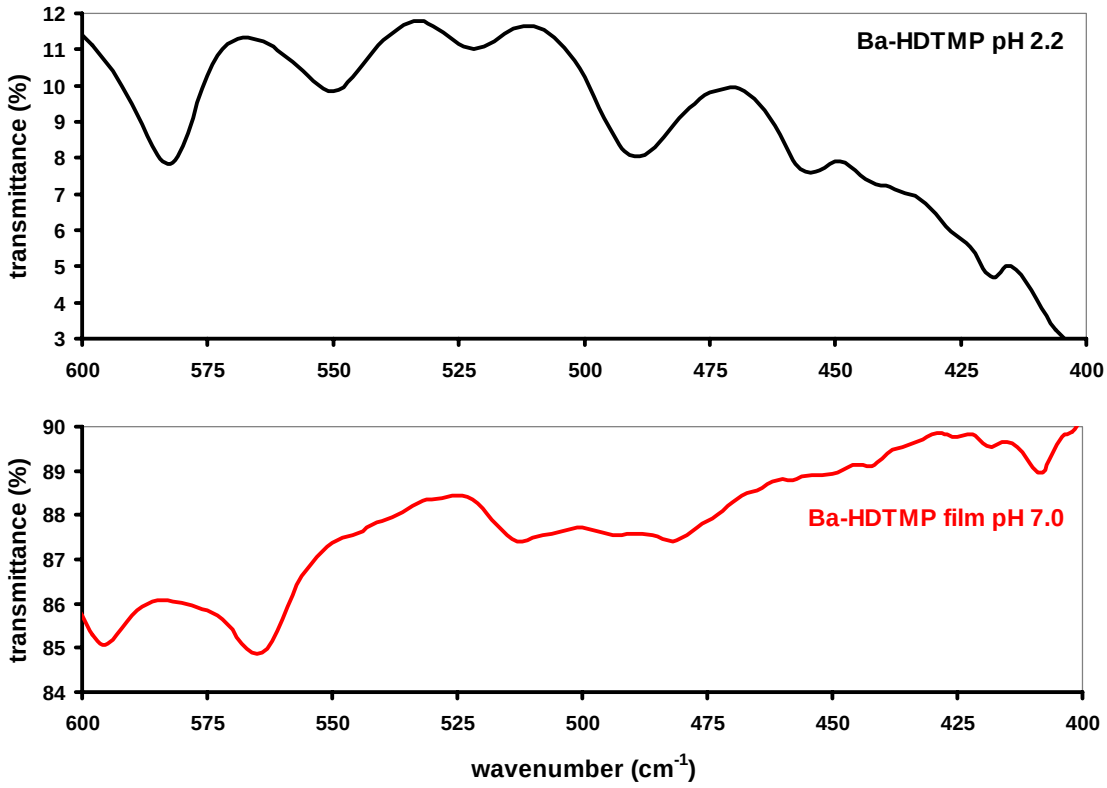


Figure S-5.10. Comparison of the the region 400-600 cm^{-1} (metal-O vibrations) of the FT-IR (in KBr pellets) of Ba-HDTMP (film at pH = 7) and Ba-HDTMP synthesized at pH 2.2.

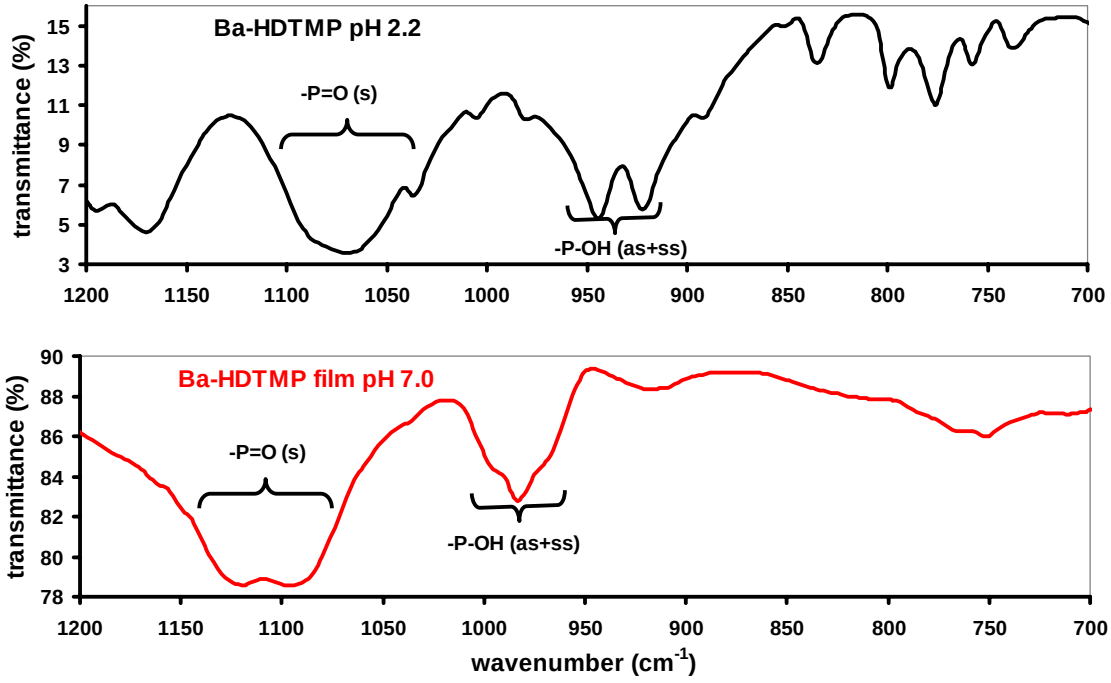


Figure S-5.11. Comparison of the the region 700-1200 cm^{-1} of the FT-IR (in KBr pellets) of Ba-HDTMP (film at pH = 7) and Ba-HDTMP synthesized at pH 2.2.

6. Corrosion Inhibition Experiments

Fig. S-6.1. Vertical Scanning Interferometry (VSI) Images

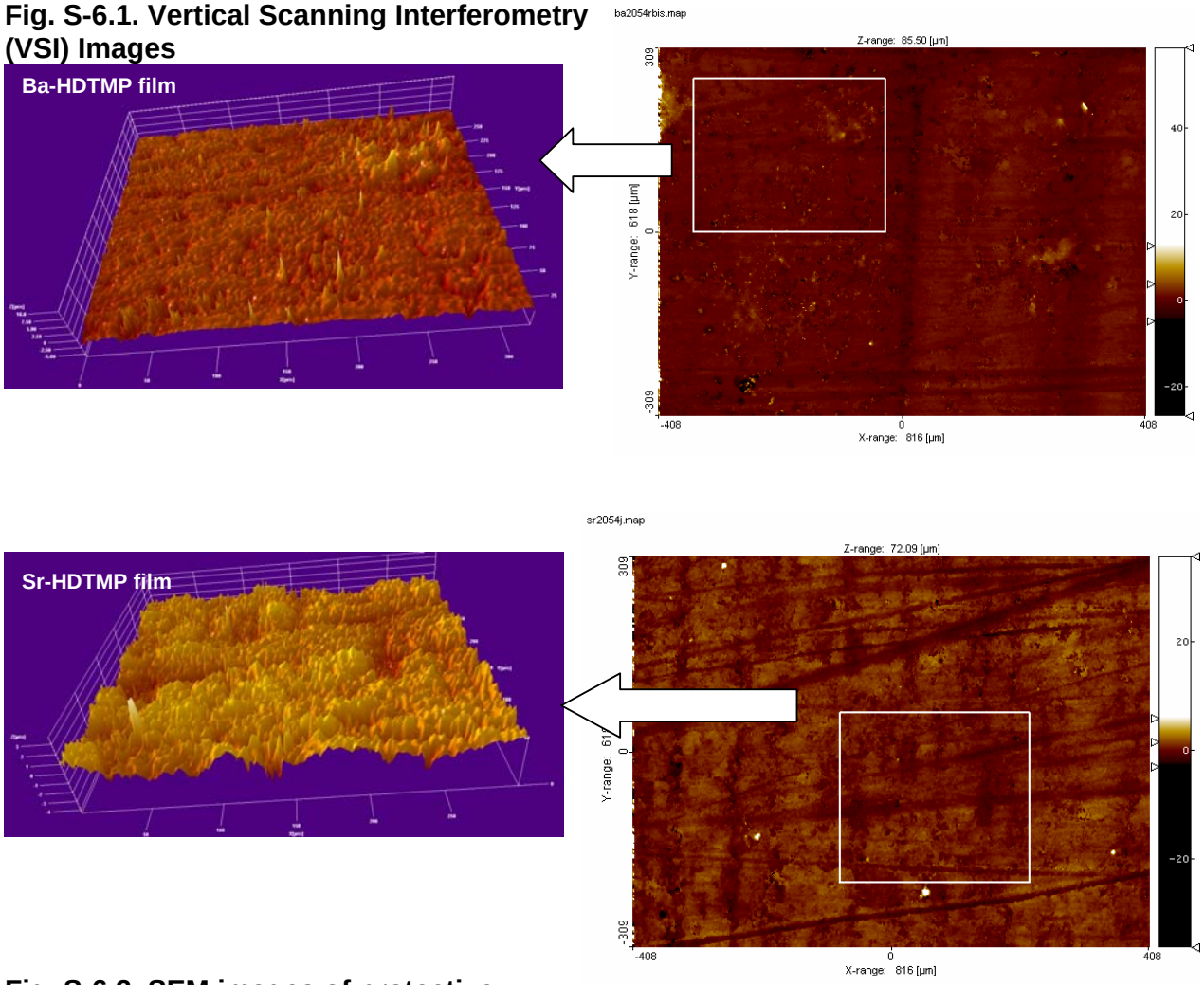
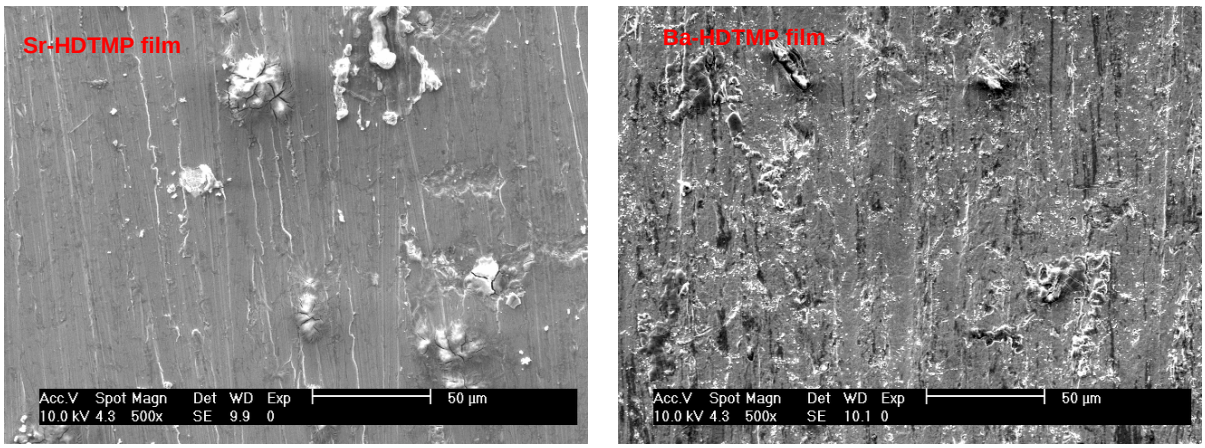


Fig. S-6.2. SEM images of protective coatings



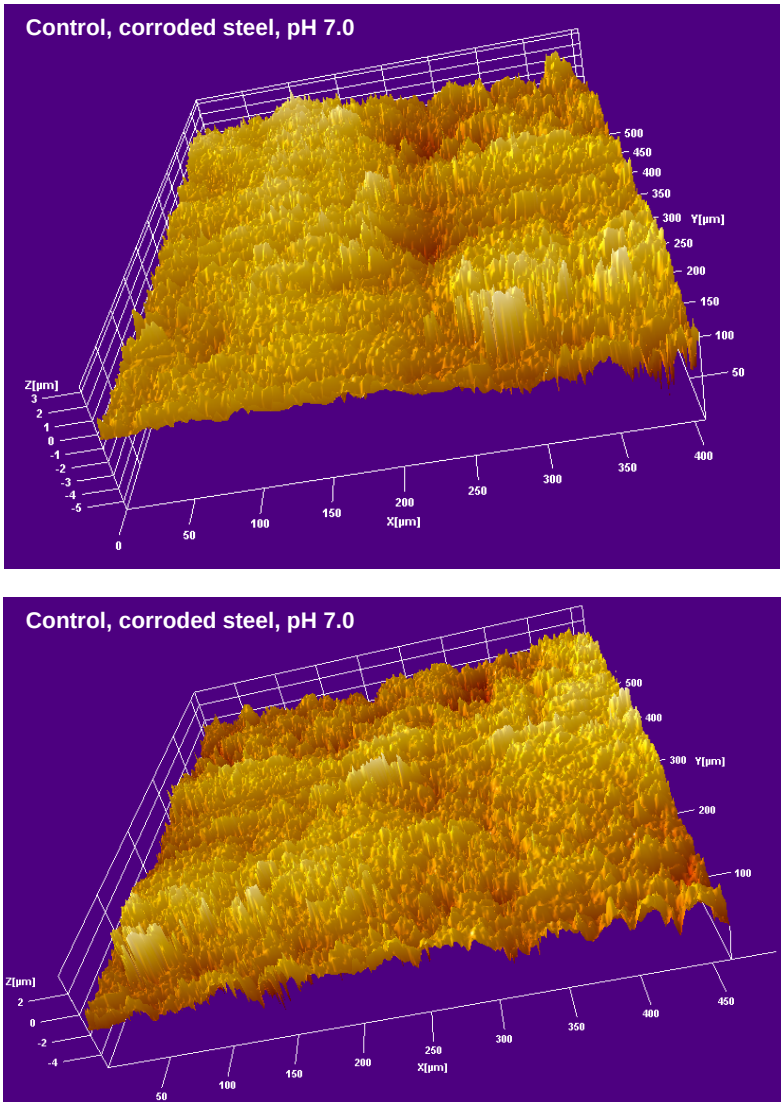


Fig. S-6.3. Vertical Scanning Interferometry (VSI) Images of "control" specimens without any anti-corrosion protection.

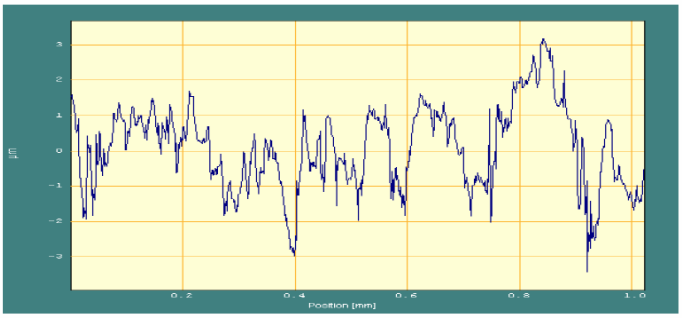
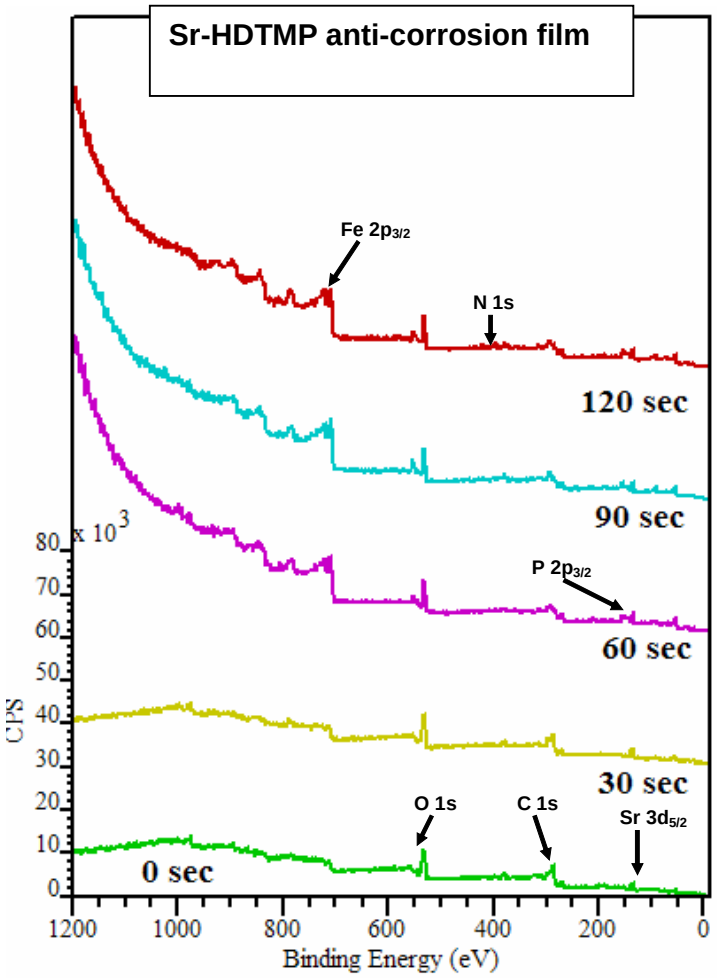


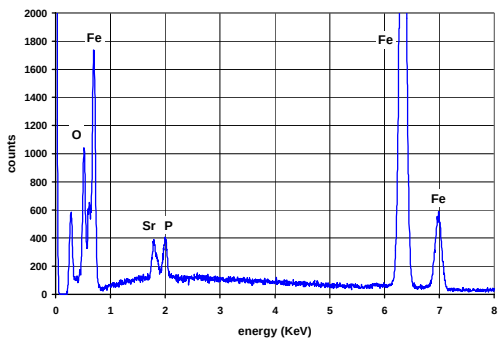
Fig. S-6.3. "Line scan" of a "control" specimen without any anti-corrosion protection.

All VSI images were acquired with a MicroXAM™ Interferoetric Surface Profiler from ADE™ Phase Shift (San Jose, CA, USA). Acquired data were processed and analysed using MapVue AE version 2.13.1 from ADE™ Phase Shift and Scanning Probe Image Processor, SPIP™ version 4.1.8.0 from Image Metrology.

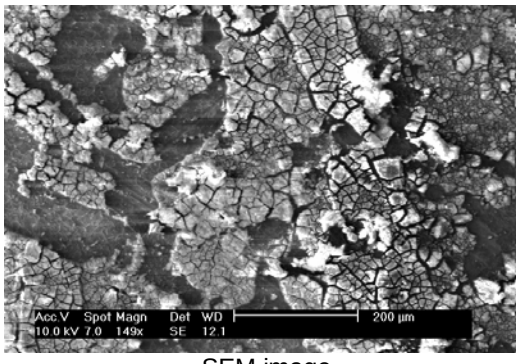
6.3. XPS Results of Metal Phosphonate Ptorective Coatings

Fig. S-6.1. Analysis of the anti-corrosion protective Sr-HDTMP film





EDX Spectrum

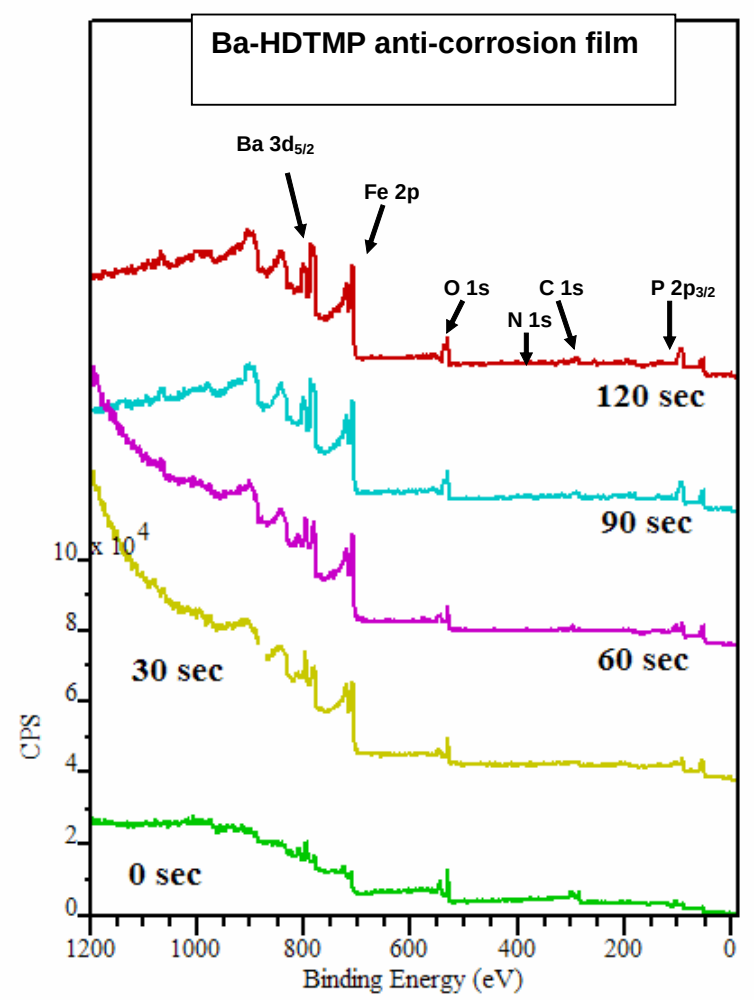


SEM image

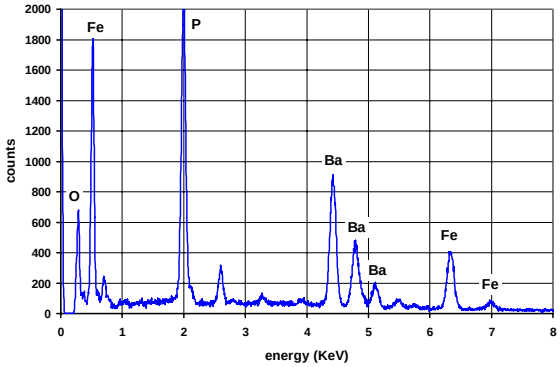
Sr-HDTMP anti-corrosion film						
Atom %	C	O	Fe	P	Sr	N
XPS at 60 sec	27.51	48.72	13.54	5.11	2.57	2.55
EDX at 15 keV	29.31	46.95	14.29	4.89	2.34	-

Fig. S-6.2. Analysis of the anti-corrosion protective Ba-HDTMP film

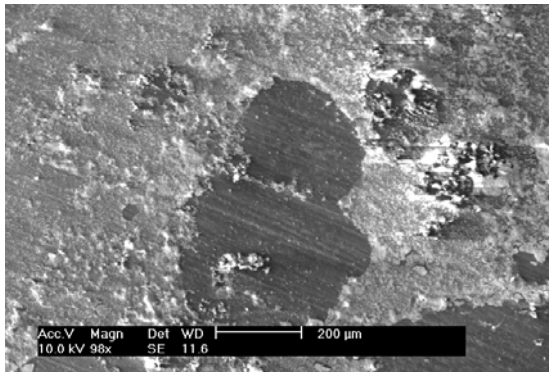
Analysis of the anti-corrosion protective Ba-HDTMP film



XPS Spectra



EDX Spectrum



SEM

Ba-HDTMP anti-corrosion film						
Atom %	C	O	Fe	P	Ba	N
XPS at 60 sec	30.51	36.29	13.54	10.12	4.99	4.75
EDX at 15 keV	32.24	34.95	15.29	11.89	5.89	-

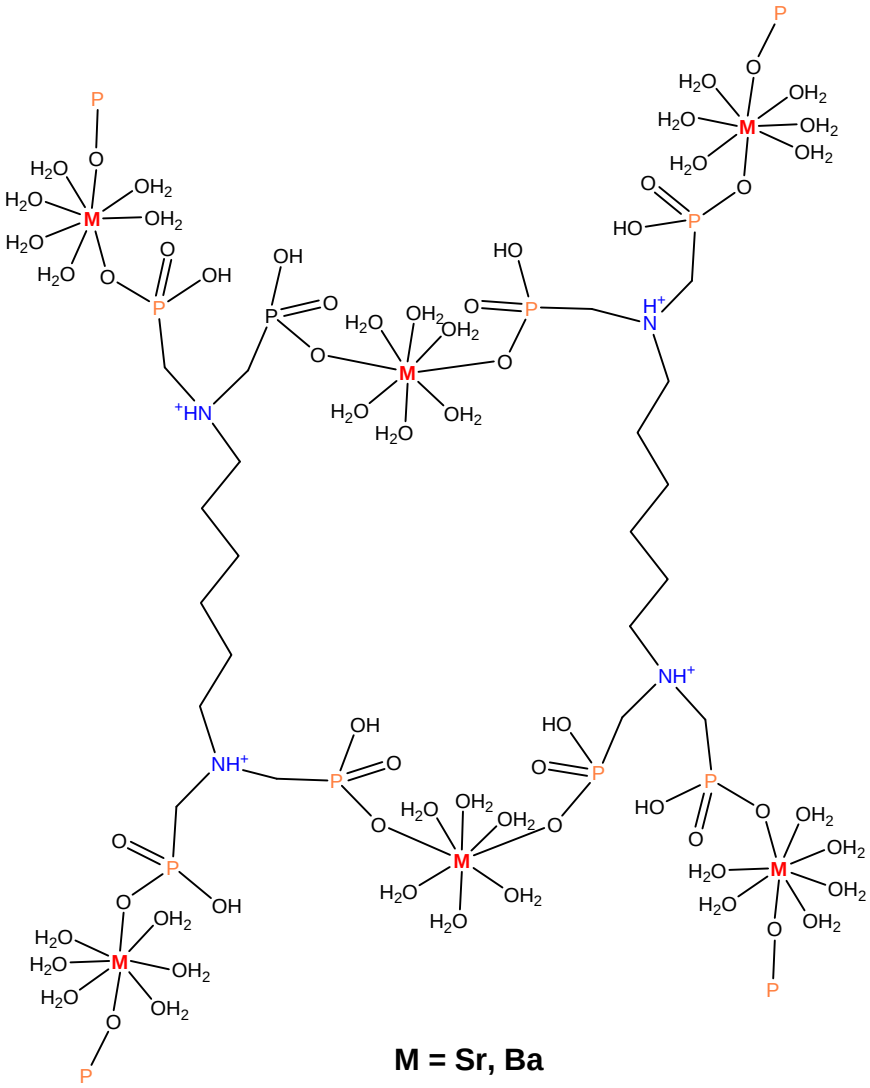


Fig. S-6.3. Proposed “ladder-type” metal-HDTMP (metal = Sr, Ba) structure formed as a protective coating on the steel specimens.

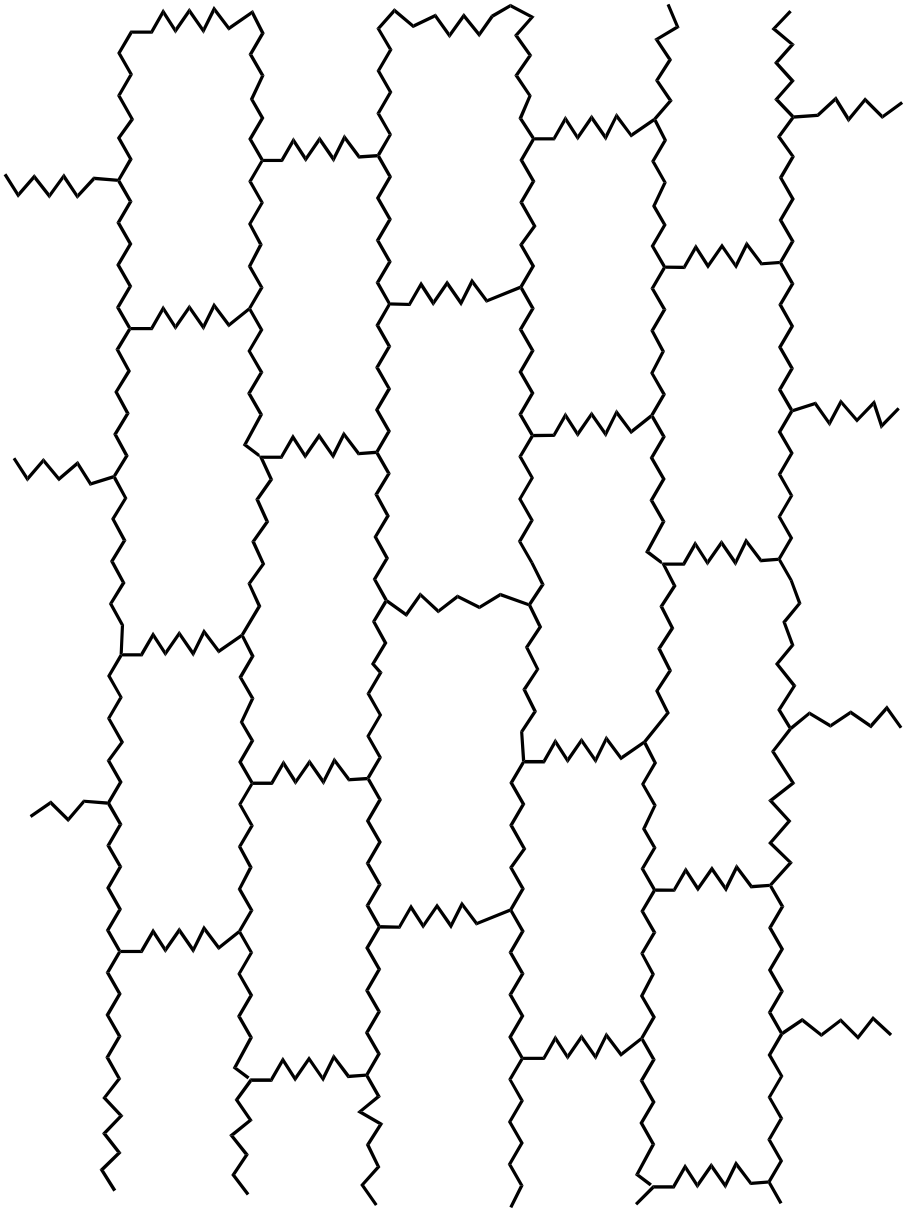
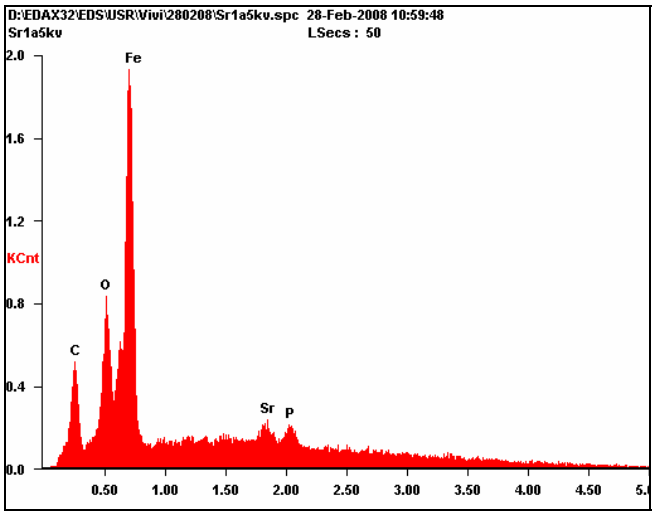


Fig. S-6.4. Proposed “ladder-type” metal-HDTMP (metal = Sr, Ba) structure formed as a protective coating on the steel specimens. The “nodes” are N atoms.

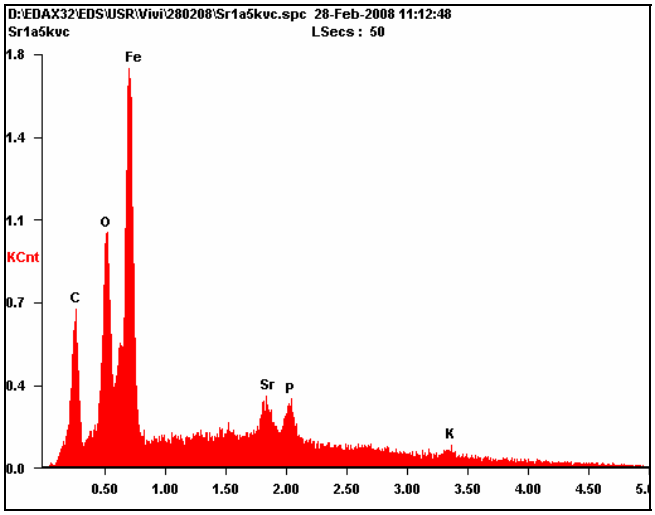
6.4. EDS Results of Metal Phosphonate Protective Coatings

Fig. S-6.5. Sr-HDTMP Protective Film



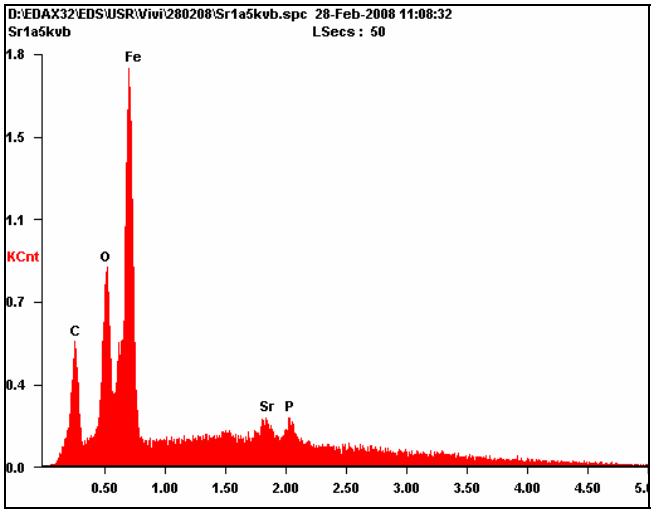
D:\EDAX32\EDS\USR\VIVI\280208\SR1A5KVB. KV: 5.00 TILT: 0.00 TAKE-OFF:35.00 AMPT:100.0 DETECTOR TYPE :SUTW-SAPPHIRE

Element	Wt %	At %
C K	08.90	27.83
O K	06.12	14.37
FeL	75.40	50.70
SrL	05.76	02.47
P K	03.82	04.63



D:\EDAX32\EDS\USR\VIVI\280208\SR1A5KVC. KV: 5.00 TILT: 0.00 TAKE-OFF:35.00 AMPT:100.0 DETECTOR TYPE :SUTW-SAPPHIRE

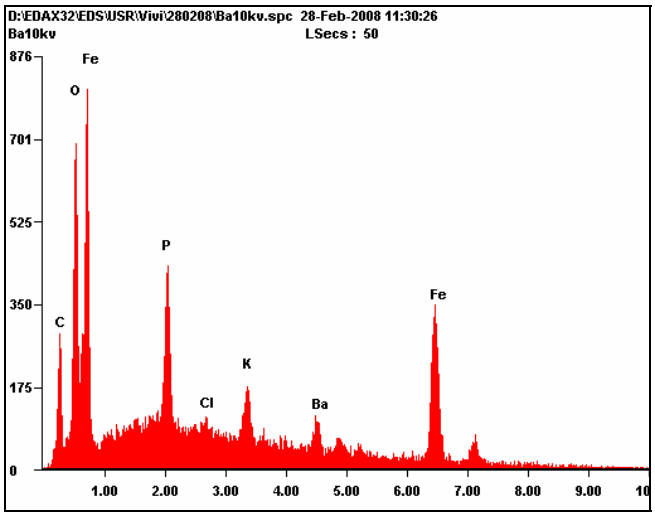
Element	Wt %	At %
C K	10.30	29.88
O K	07.56	16.46
FeL	60.22	37.57
SrL	09.58	03.81
P K	05.45	06.13



D:\EDAX32\EDS\USR\VIVI\280208\SR1A5KVB. KV: 5.00 TILT: 0.00 TAKE-OFF:35.00 AMPT:100.0 DETECTOR TYPE :SUTW-SAPPHIRE

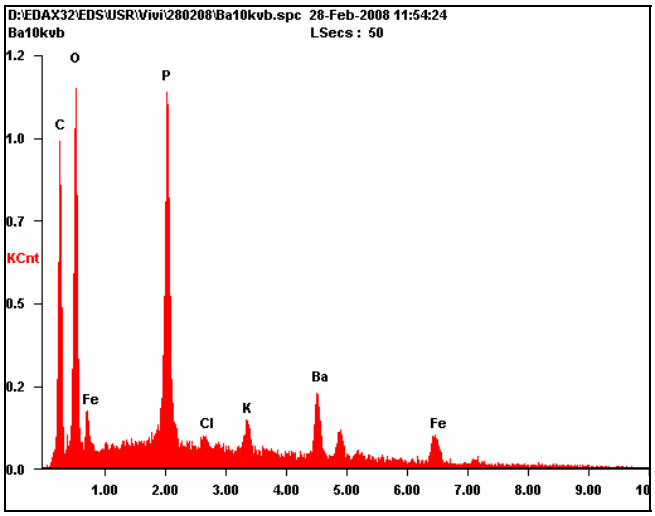
Element	Wt %	At %
C K	10.13	30.16
O K	07.33	16.39
FeL	71.75	45.94
SrL	06.60	02.69
P K	04.18	04.82

Fig. S-6.6. Ba-HDTMP Protective Film



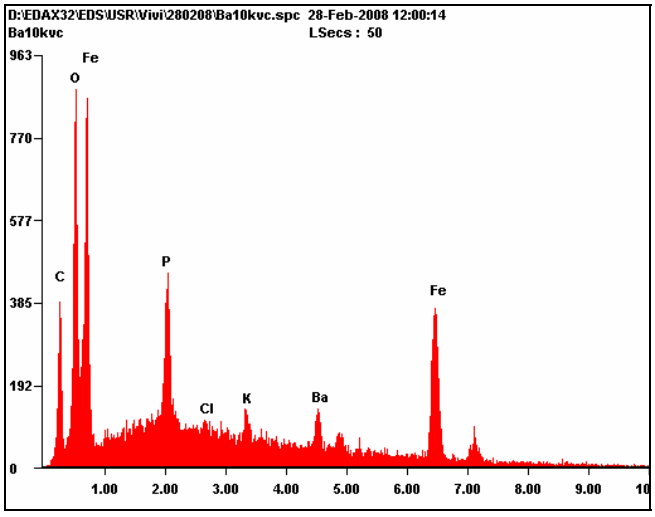
D:\EDAX32\EDS\USR\VIVI\280208\BA10KV.SP KV:10.00 TILT: 0.00 TAKE-OFF:35.00 AMPT:100.0 DETECTOR TYPE :SUTW-SAPPHIRE

Element	Wt %	At %
C K	12.40	34.21
O K	10.54	21.84
FeL	43.12	25.59
P K	07.57	08.10
BaL	20.11	04.85



D:\EDAX32\EDS\USR\VIVI\280208\BA10KVB.S KV:10.00 TILT: 0.00 TAKE-OFF:35.00 AMPT:100.0 DETECTOR TYPE :SUTW-SAPPHIRE

Element	Wt %	At %
C K	28.33	57.80
O K	12.80	19.60
FeL	06.36	02.79
P K	14.74	11.66
BaL	34.73	06.20



D:\EDAX32\EDS\USR\VIVI\280208\BA10KVC.S KV:10.00 TILT: 0.00 TAKE-OFF:35.00 AMPT:100.0 DETECTOR TYPE :SUTW-SAPPHIRE

Element	Wt %	At %
C K	15.44	40.43
O K	10.82	21.28
FeL	40.73	22.94
P K	07.16	07.27
BaL	22.24	05.09

6.5. Characterization of the metal phosphonate protective films by FT-IR spectrocsopy

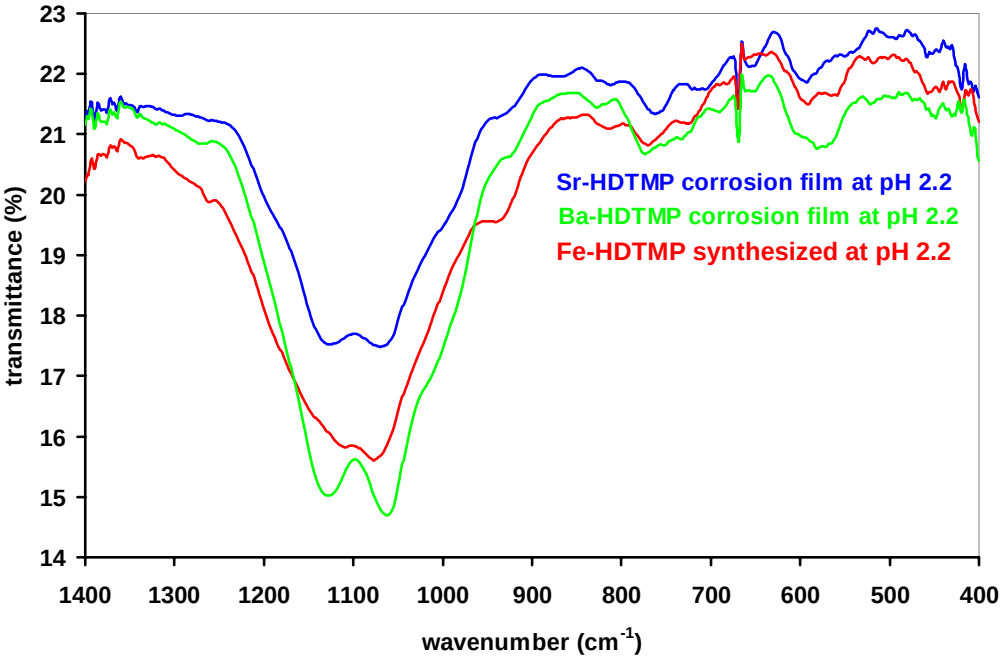


Figure S-6.7. FT-IR (in KBr pellets) of Sr-HDTMP and Ba-HDTMP corrosion film and comparison with the FT-IR of Fe-HDTMP synthesized at pH 2.2. The phosphonate spectral region is shown.

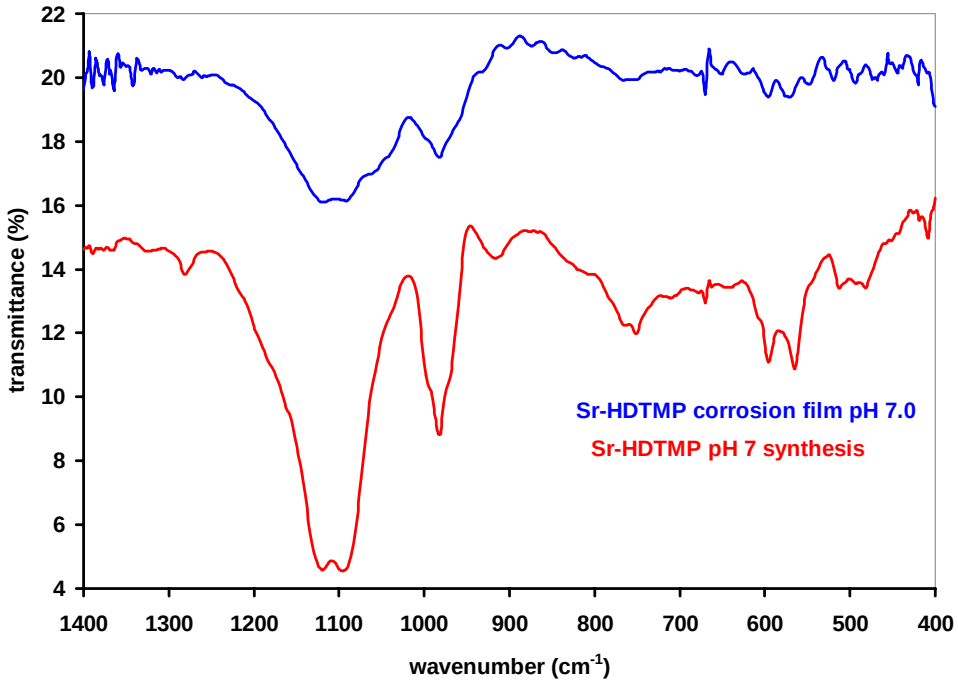


Figure S-6.8. FT-IR (in KBr pellets) of Sr-HDTMP corrosion film at pH 7 and comparison with the FT-IR of Sr-HDTMP synthesized at pH 7.

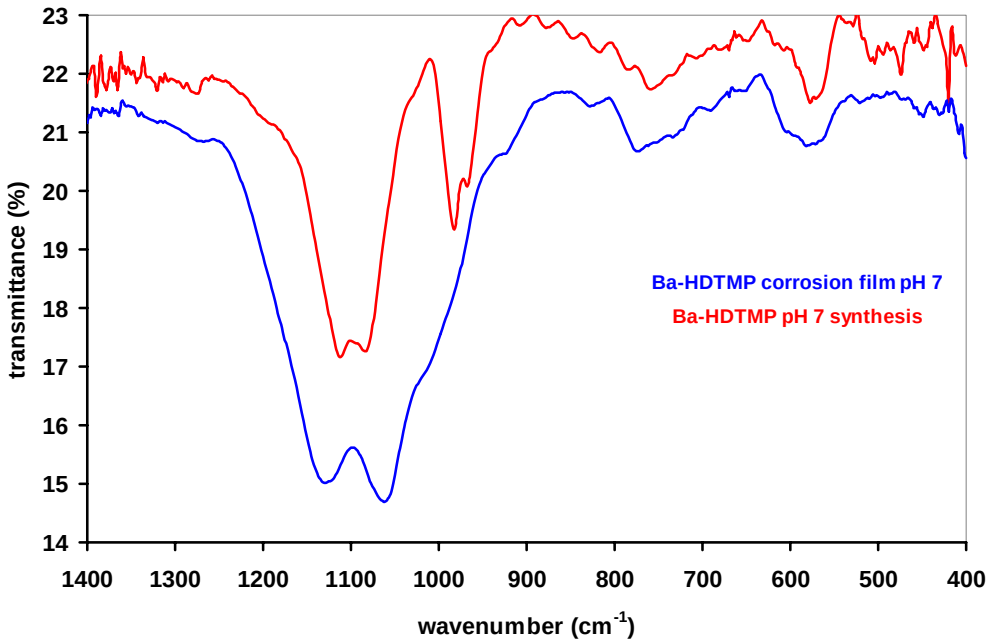


Figure S-6.9. FT-IR (in KBr pellets) of Ba-HDTMP corrosion film at pH 7 and comparison with the FT-IR of Ba-HDTMP synthesized at pH 7.

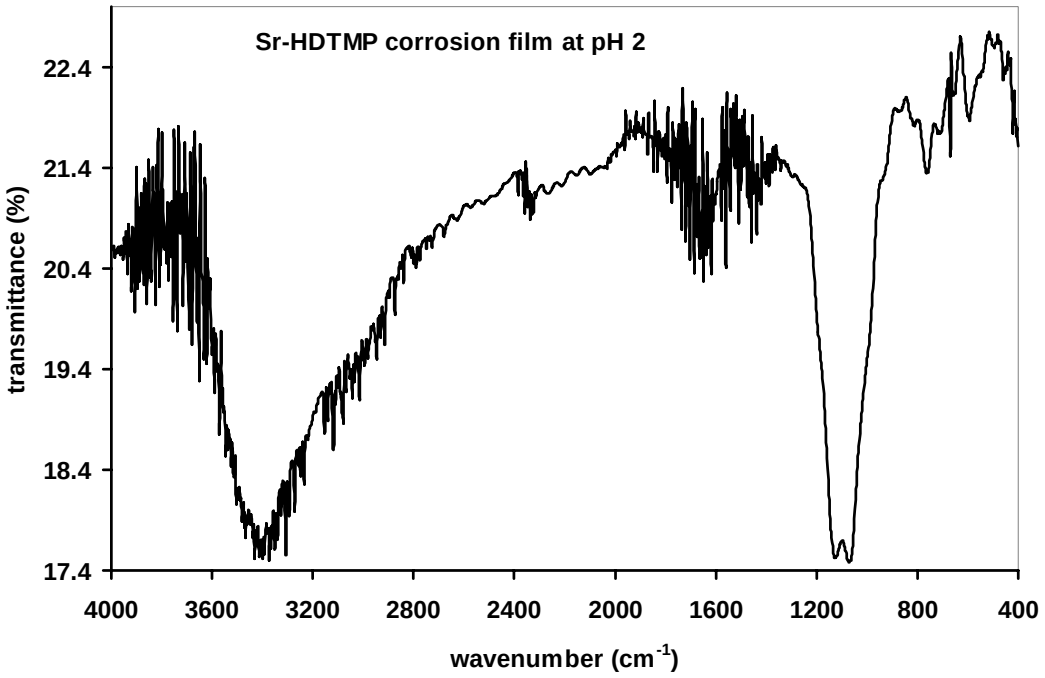


Figure S-6.10. FT-IR (in KBr pellets) of corrosion film at pH 2.2 from Sr+HDTMP. This film is actually does not contain Sr, but is composed of Fe-HDTMP.

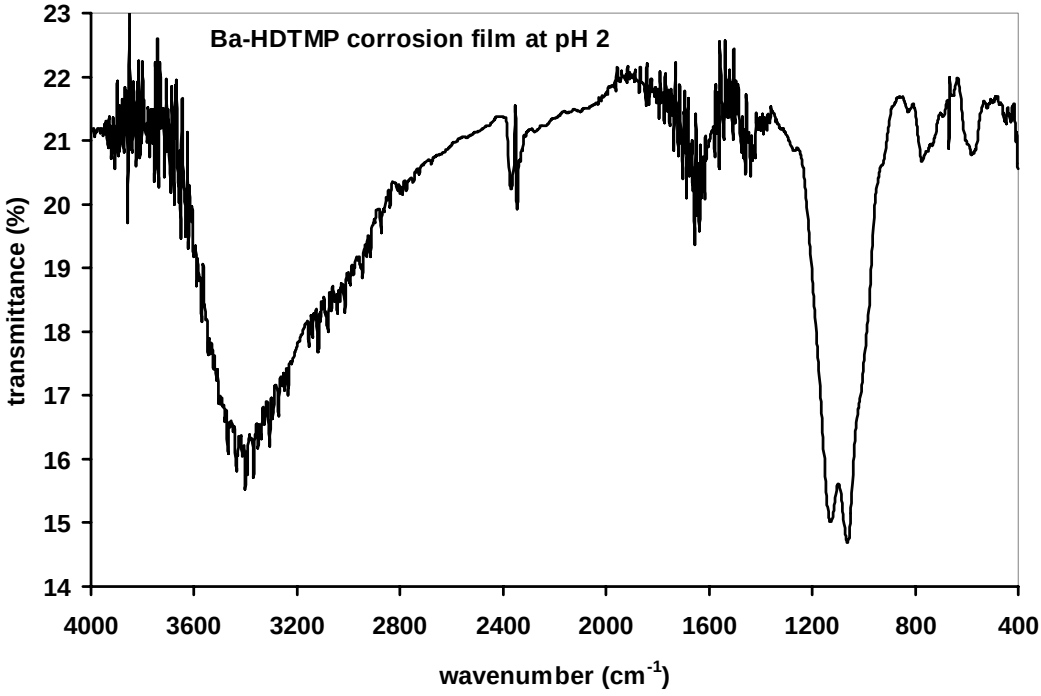


Figure S-6.11. FT-IR (in KBr pellets) of corrosion film at pH 2.2 from Ba+HDTMP. This film is actually does not contain Ba, but is composed of Fe-HDTMP.

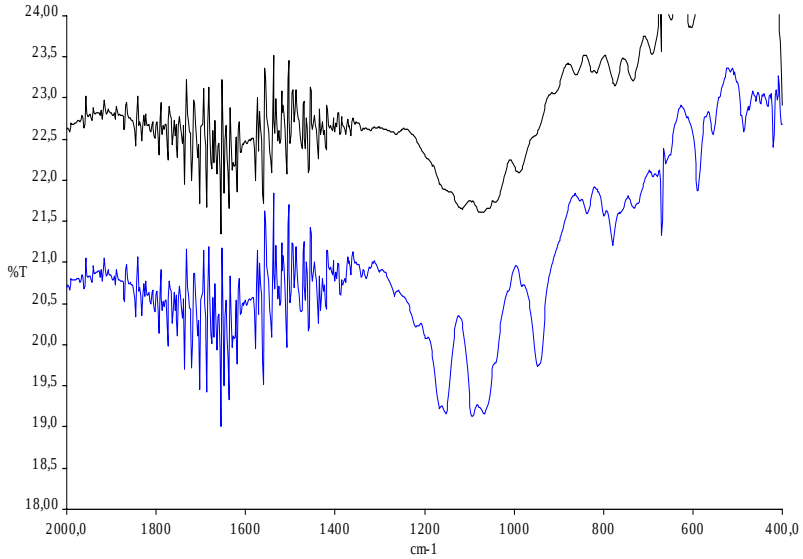


Figure S-6.12. FT-IR (in KBr pellets) of corrosion film on a copper specimen at pH 2.2 from added HDTMP. Black: Cu-HDTMP film on corrosion coupons. Blue: As synthesized Cu-HDTMP

7. Miscellaneous Views of the Structures

7.1. (en)(HDTMP)($2H_2O$)

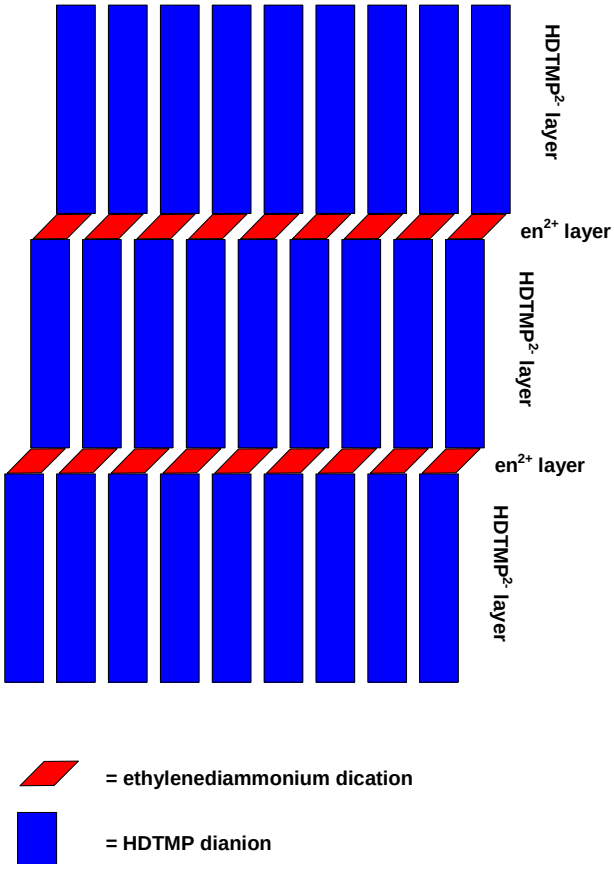


Figure S-7.1. Layered structure of (en)(HDTMP)($2H_2O$).

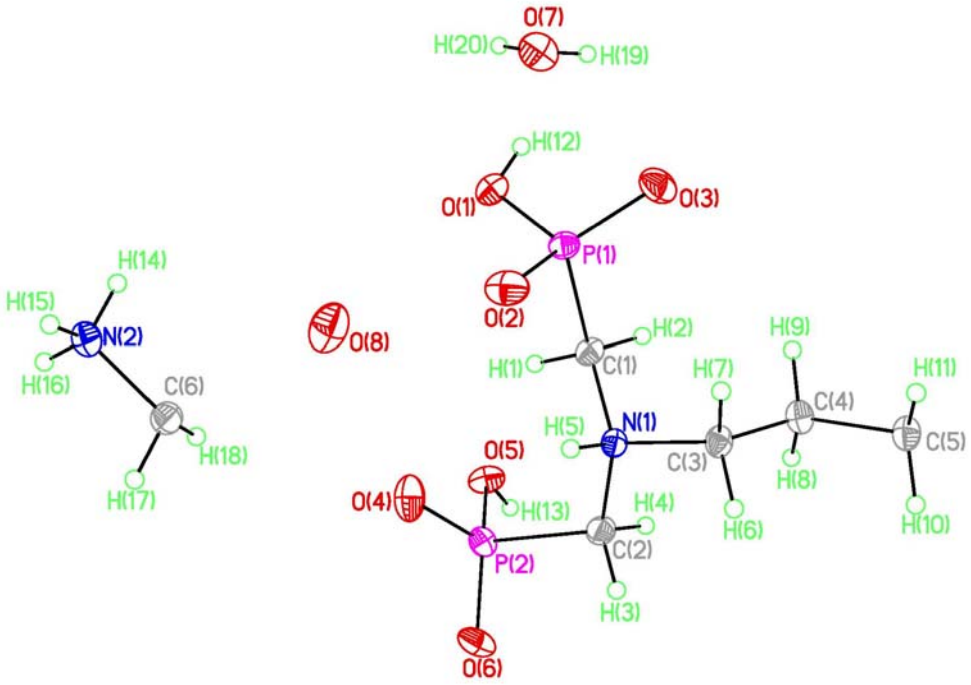


Figure S-7.2. Asymmetric unit in the structure of (en)(HDTMP)·2H_2O

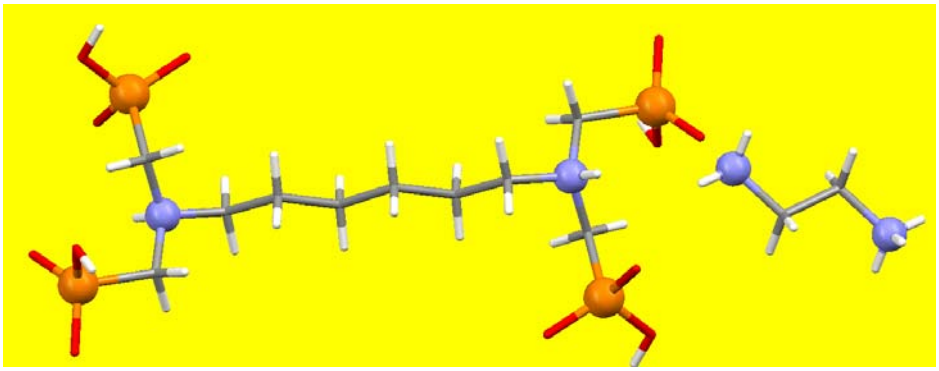


Figure S-7.3. A view of one molecule of en and one molecule of HDTMP (water molecules omitted)

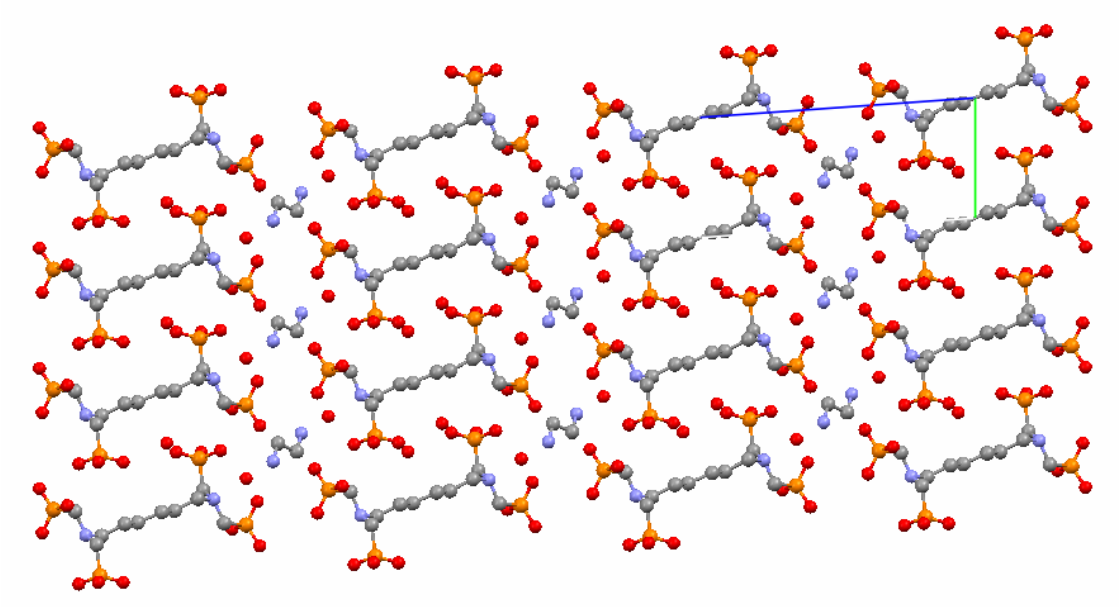


Figure S-7.4. Packing along a-axis

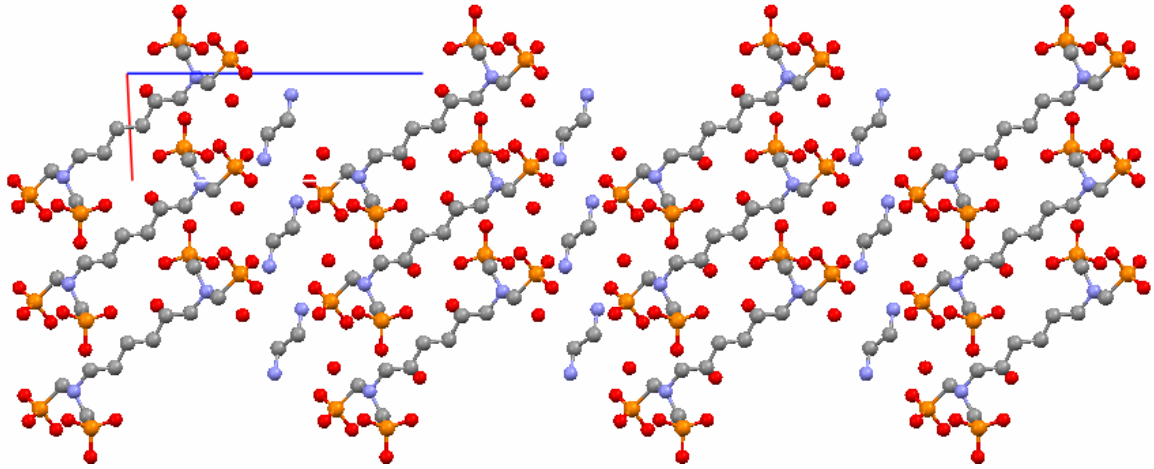


Figure S-7.5. Packing along b-axis

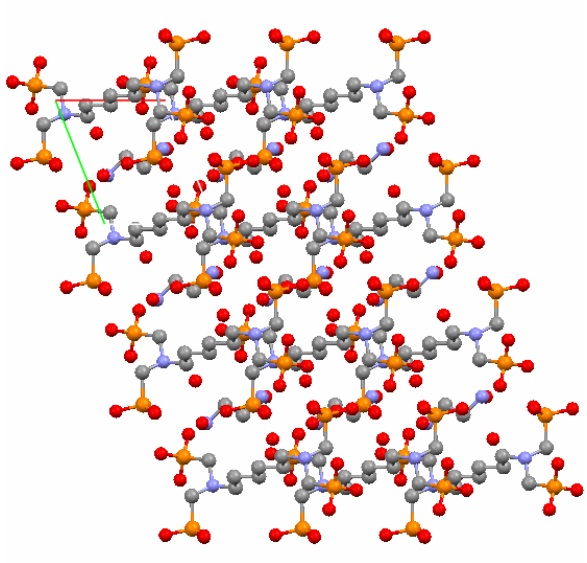


Figure S-7.6. Packing along c-axis

Hydrogen Bonding Scheme (a-axis) for (en)(HDTMP)

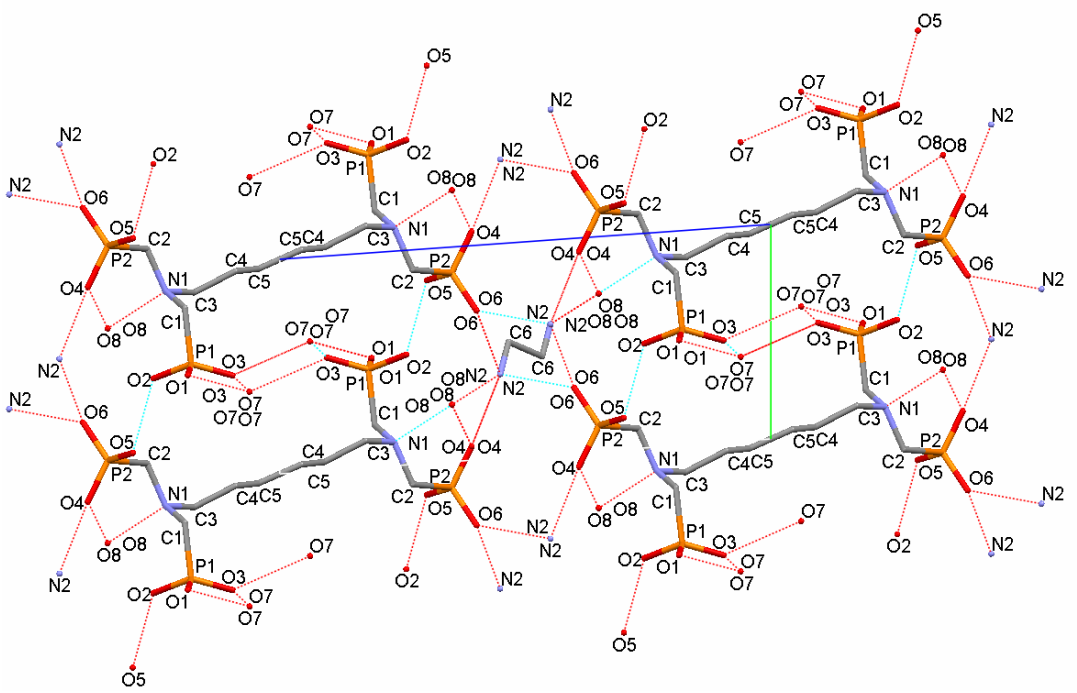


Figure S-7.7. Hydrogen Bonding Scheme (b-axis) for (en)(HDTMP)

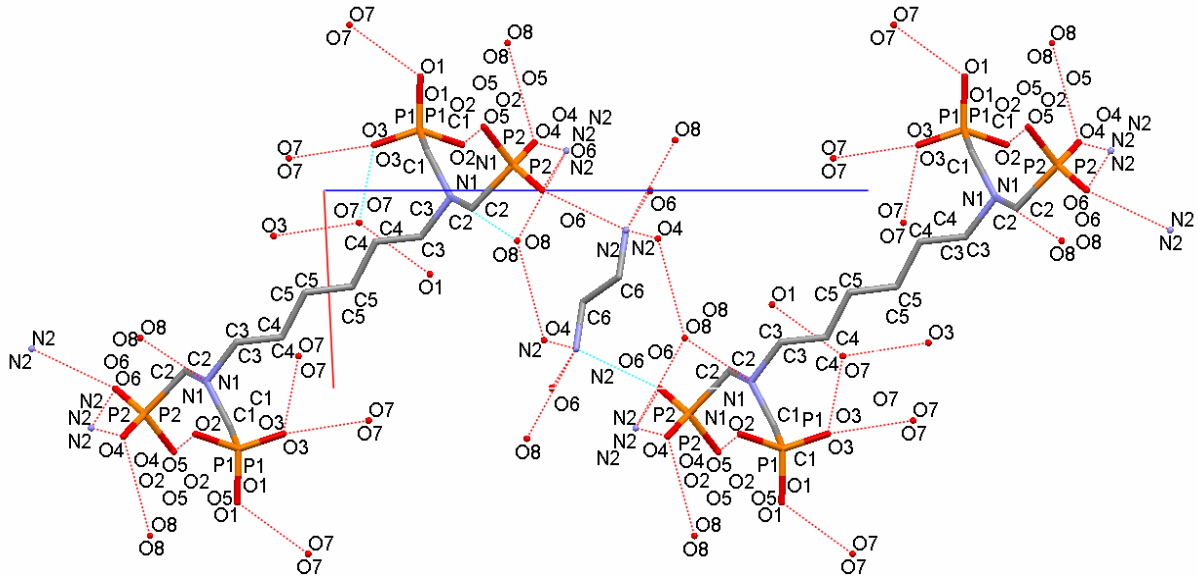


Figure S-7.8. Hydrogen Bonding Scheme (c-axis) for (en)(HDTMP)

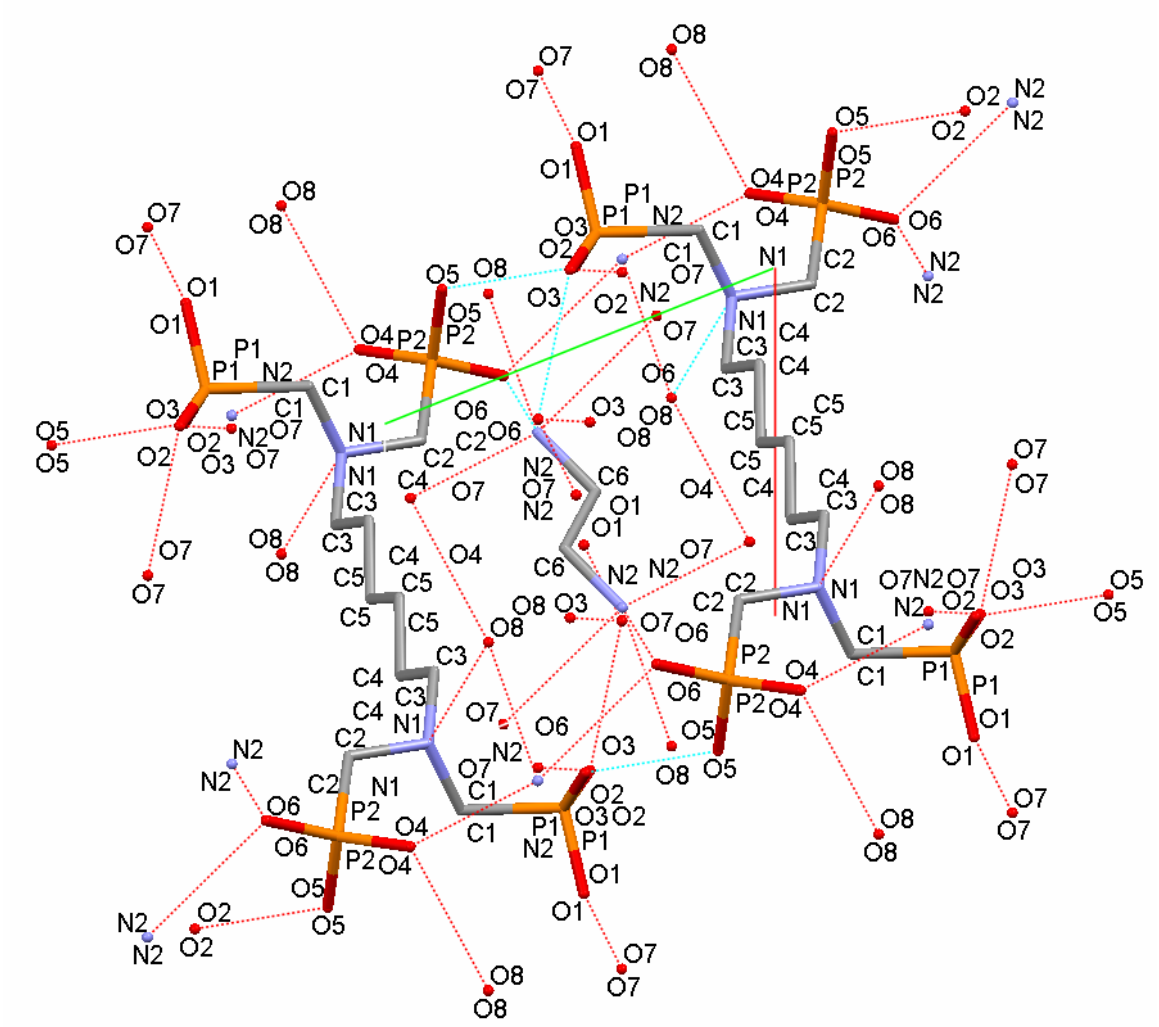


Figure S-7.9. Another view of the Hydrogen Bonding Scheme for (en)(HDTMP)

7.2. {Sr[(HDTMP)(H_2O)$_6$]·2H_2O} (Sr-HDTMP, 1)

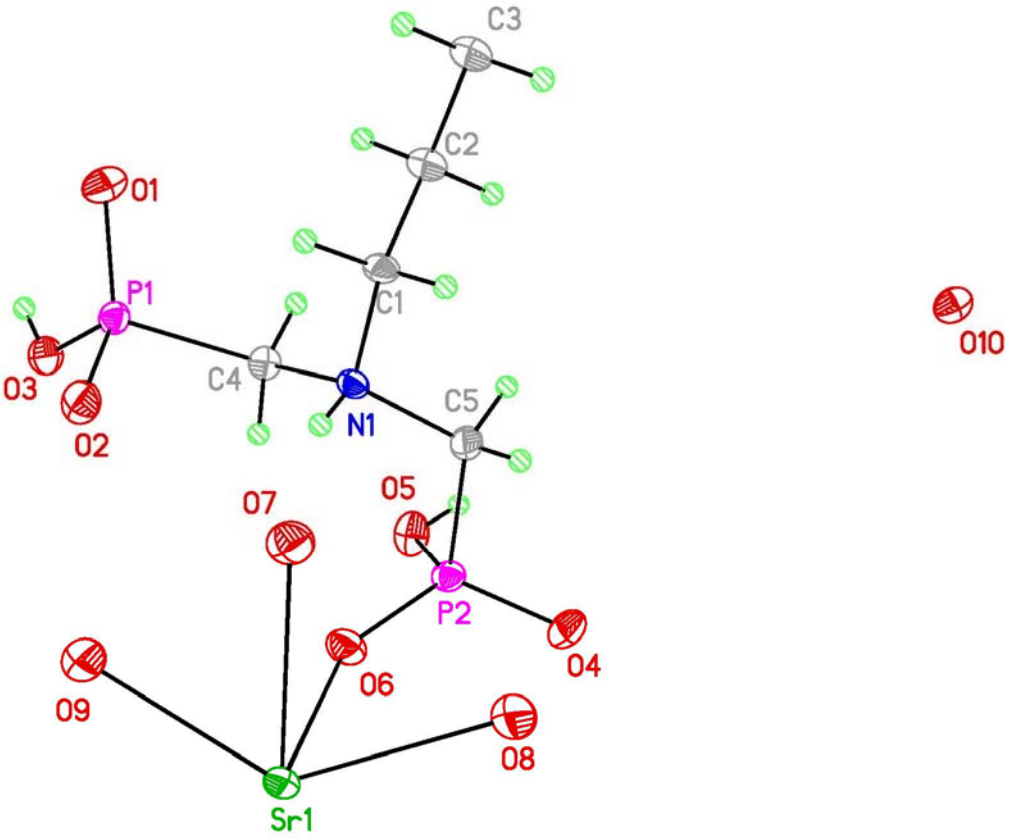


Figure S-7.10. Asymmetric unit in the structure of {Sr[(HDTMP)(H_2O)$_6$]·2H_2O} (Sr-HDTMP, 1)

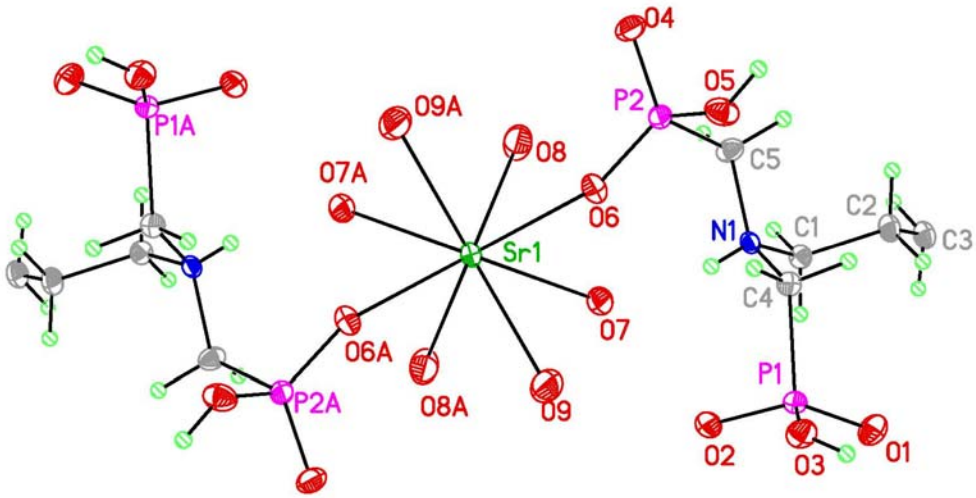


Figure S-7.11. Coordination environment of Sr in the structure of {Sr[(HDTMP)(H_2O)$_6$]·2H_2O} (Sr-HDTMP, 1)

Figure S-7.12. Zig-Zag chains in the structure of {Sr[(HDTMP)(H_2O)$_6$]·2H_2O} (Sr-HDTMP, 1)

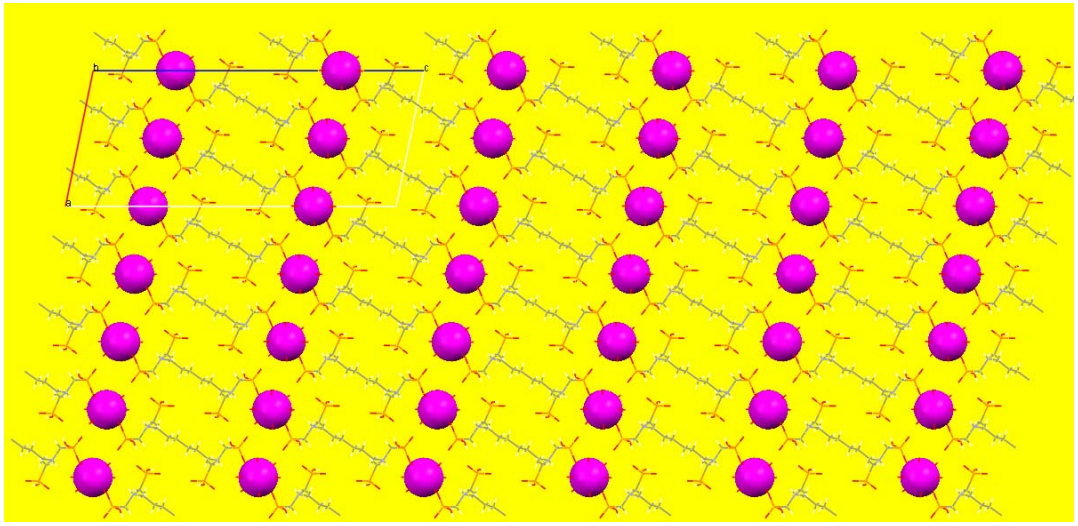


Figure S-7.13. View of a layer along b-axis in the structure of {Sr[(HDTMP)(H_2O)$_6$]·2H_2O} (Sr-HDTMP, 1)

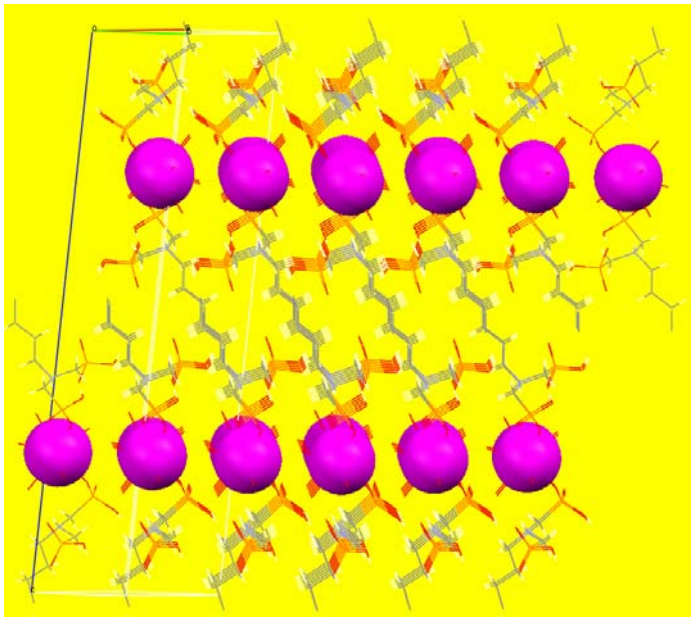


Figure S-7.14. Zig-Zag chains in the structure of {Sr[(HDTMP)(H_2O)$_6$]·2H_2O} (Sr-HDTMP, 1)

7.3. {Ba[(HDTMP)(H_2O)$_6$]·2H_2O} (Ba-HDTMP, 2)

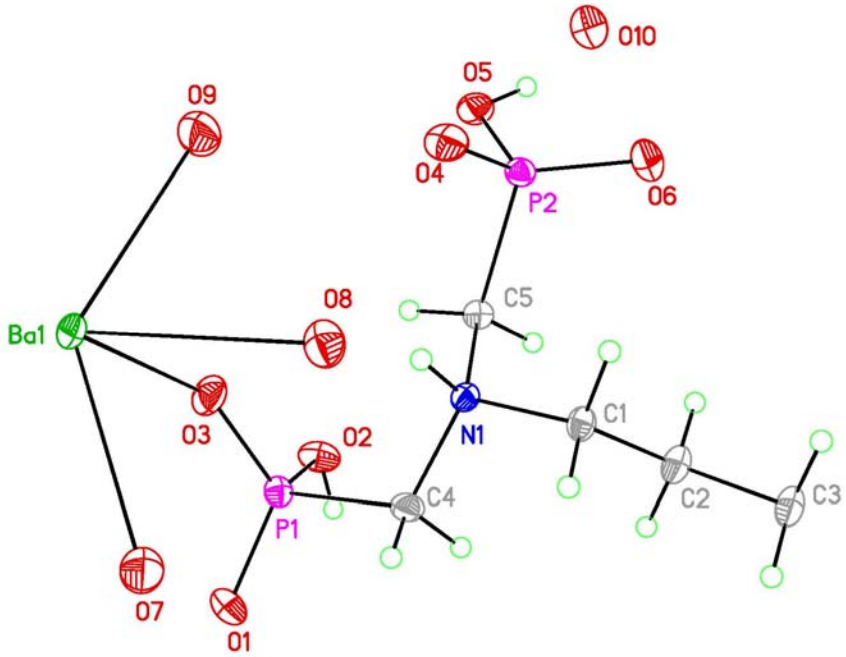


Figure S-7.15. Asymmetric unit in the structure of {Ba[(HDTMP)(H_2O)$_6$]·2H_2O} (Ba-HDTMP, 2)

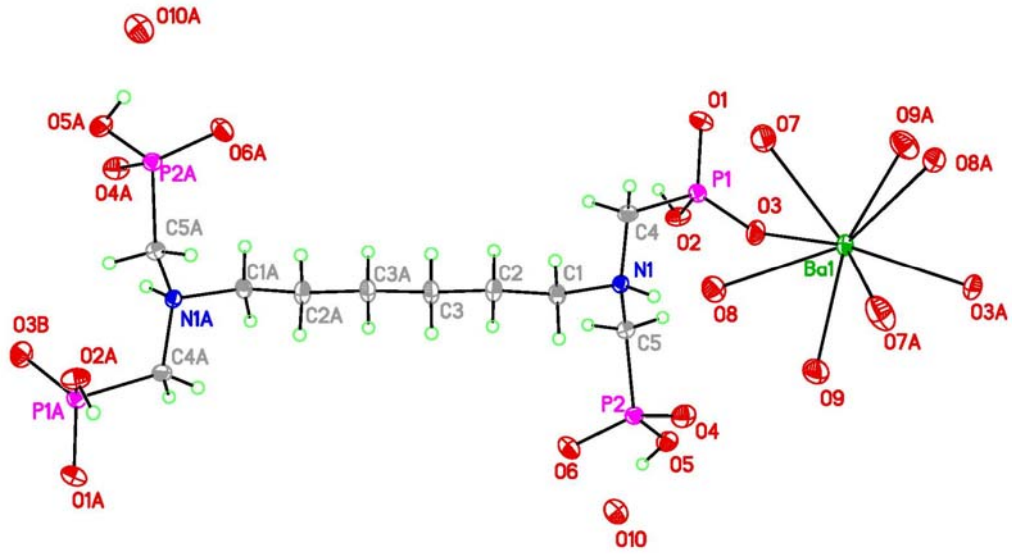


Figure S-7.16. Coordination environment of Ba in the structure of {Ba[(HDTMP)(H_2O)$_6$]·2H_2O} (Ba-HDTMP, 2)

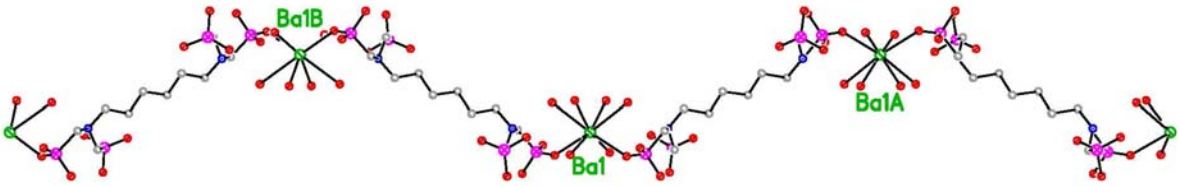


Figure S-7.17. Zig-Zag chains in the structure of {Ba[(HDTMP)(H_2O)$_6$]·2H_2O} (Ba-HDTMP, 2)

7.3. {Cu[(HDTMP)(H_2O)$_4$]·6H_2O} (Cu-HDTMP, 3)

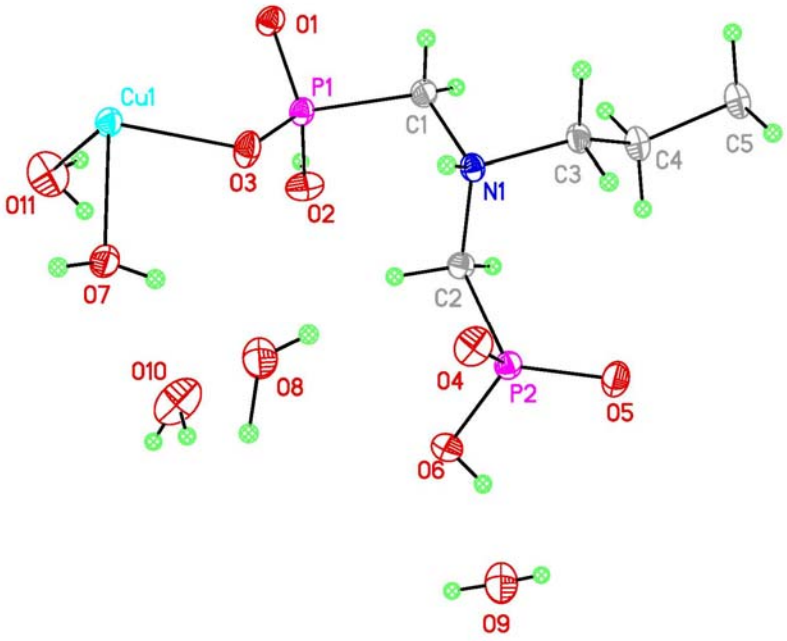


Figure S-7.18. Asymmetric unit in the structure of {Cu[(HDTMP)(H_2O)$_4$]·6H_2O} (Cu-HDTMP, 3)

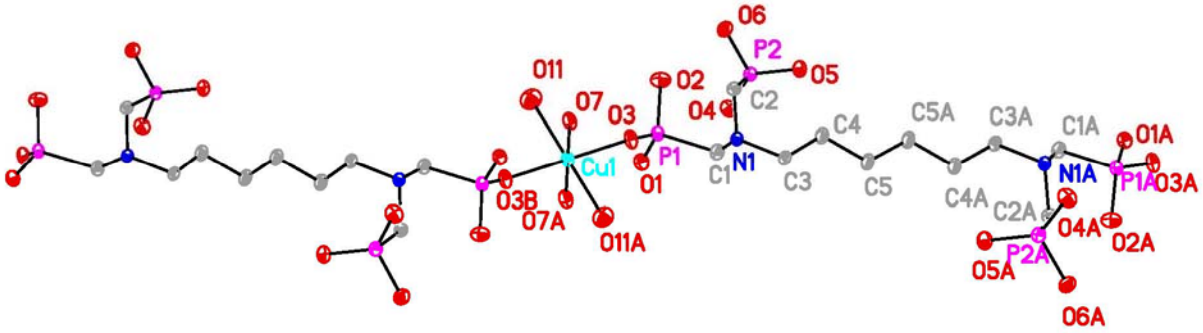


Figure S-7.19. Coordination environment of Ba in the structure of {Cu[(HDTMP)(H_2O)$_4$]·6H_2O} (Cu-HDTMP, 3)

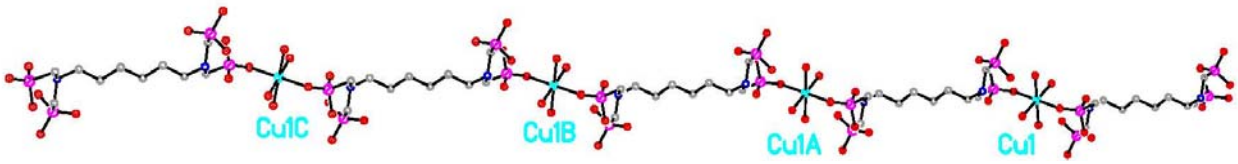


Figure S-7.20. A linear "Cu-HDTMP" chain in the structure of {Cu[(HDTMP)(H_2O)$_4$]·6H_2O} (Cu-HDTMP, 3)

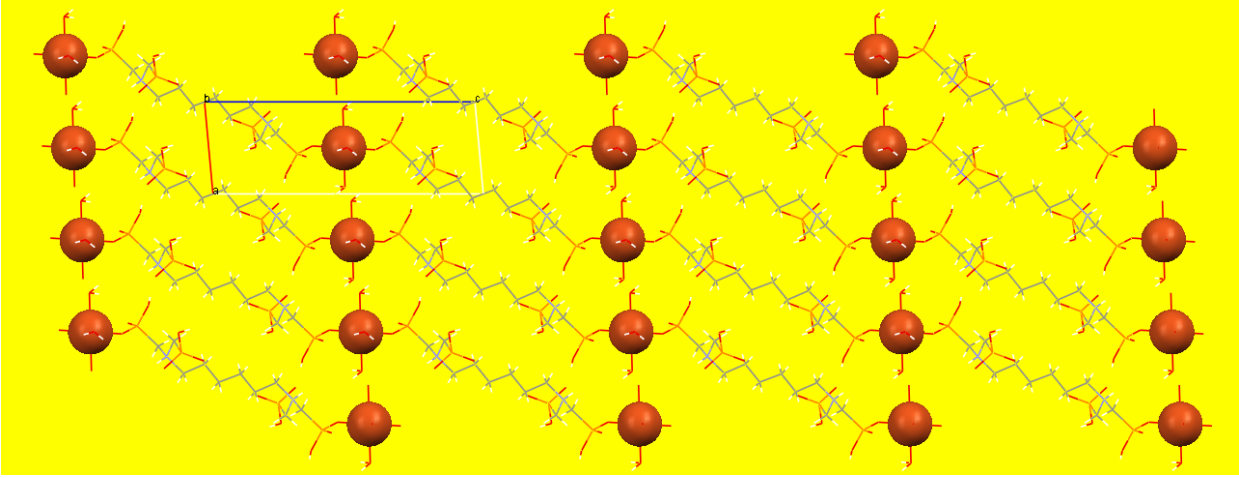


Figure S-7.21. Linear chains viewed along b-axis in the structure of {Cu[(HDTMP)(H_2O)$_4$]·6H_2O} (Cu-HDTMP, 3)

8. X-ray Structural Data

8.1. (en)(HDTMP)($2H_2O$)

Table 8.1.1. Crystal data and structure refinement for (en)(HDTMP)

	(en)(HDTMP)
Empirical formula	$C_6H_{20}N_2O_8P_2$
Formula weight	310.18
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a (Å)	6.1950(11)
b (Å)	7.4889(13)
c (Å)	15.955 (3)
α (deg)	84.472(3)
β (deg)	85.319(3)
γ (deg)	67.881(3)
Volume ($Å^3$)	681.7(2)
Z	2
Density (calc.) ($g \cdot cm^{-3}$)	1.511
Absorption coefficient (mm^{-1})	0.352
F(000)	328
Crystal size (mm)	0.22 x 0.20 x 0.16
θ range for data collection (deg)	1.28 to 28.28
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 9$, $-21 \le l \le 17$
Reflections collected	4795
Independent reflections	3056 [R(int) = 0.0185]
Independent reflections [$I > 2\sigma(I)$]	3056
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3056 / 0 / 176
Goodness-of-fit on F^2	1.073
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0566, $wR2$ = 0.1614
R indices (all data)	$R1$ = 0.0711, $wR2$ = 0.1691
Largest diff. peak and hole (e $Å^{-3}$)	1.870 and –0.505

Table 8.1.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for (en)(HDTMP). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	8040(5)	1947(4)	1934(2)	25(1)
C(2)	10886(6)	-927(4)	2704(2)	31(1)
C(3)	12334(5)	1263(4)	1743(2)	26(1)
C(4)	12585(6)	407(5)	904(2)	30(1)
C(5)	14849(6)	370(5)	436(2)	30(1)
C(6)	4360(6)	4603(5)	5342(2)	32(1)
N(1)	10339(4)	1105(3)	2327(2)	23(1)
N(2)	2002(5)	6082(4)	5512(2)	31(1)
O(1)	4237(4)	5098(3)	1871(2)	37(1)
O(2)	7685(5)	5139(3)	2576(2)	42(1)
O(3)	7696(4)	5256(4)	965(2)	40(1)
O(4)	7574(5)	653(4)	3908(2)	43(1)
O(5)	6784(4)	-1465(3)	2992(2)	33(1)
O(6)	9983(4)	-3042(4)	4006(2)	38(1)
O(7)	1627(6)	6073(5)	616(2)	48(1)
O(8)	2544(6)	2655(5)	3505(2)	71(1)
P(1)	6937(1)	4581(1)	1804(1)	25(1)
P(2)	8710(1)	-1208(1)	3498(1)	26(1)

Table 8.1.3. Bond lengths [A] and angles [deg] for (en)(HDTMP).

C(1)-N(1)	1.488(4)
C(1)-P(1)	1.825(3)
C(1)-H(1)	0.9700
C(1)-H(2)	0.9700
C(2)-N(1)	1.504(4)
C(2)-P(2)	1.830(3)
C(2)-H(3)	0.9700
C(2)-H(4)	0.9700
C(3)-C(4)	1.510(4)
C(3)-N(1)	1.521(4)
C(3)-H(7)	0.9700
C(3)-H(6)	0.9700
C(4)-C(5)	1.526(4)
C(4)-H(9)	0.9700
C(4)-H(8)	0.9700
C(5)-C(5)#1	1.519(6)
C(5)-H(11)	0.9700
C(5)-H(10)	0.9700
C(6)-N(2)	1.486(4)
C(6)-C(6)#2	1.505(6)
C(6)-H(18)	0.9700
C(6)-H(17)	0.9700
N(1)-H(5)	0.91(4)
N(2)-H(15)	0.8900
N(2)-H(16)	0.8900
N(2)-H(14)	0.8900
O(1)-P(1)	1.565(2)
O(1)-H(12)	0.8200
O(2)-P(1)	1.498(2)
O(3)-P(1)	1.489(3)
O(4)-P(2)	1.492(3)
O(5)-P(2)	1.572(2)
O(5)-H(13)	0.8200
O(6)-P(2)	1.497(2)
O(7)-H(20)	0.89(7)
O(7)-H(19)	0.79(8)

N(1)-C(1)-P(1)	112.84(19)
N(1)-C(1)-H(1)	109.0
P(1)-C(1)-H(1)	109.0
N(1)-C(1)-H(2)	109.0
P(1)-C(1)-H(2)	109.0
H(1)-C(1)-H(2)	107.8
N(1)-C(2)-P(2)	114.5(2)
N(1)-C(2)-H(3)	108.6
P(2)-C(2)-H(3)	108.6
N(1)-C(2)-H(4)	108.6
P(2)-C(2)-H(4)	108.6
H(3)-C(2)-H(4)	107.6
C(4)-C(3)-N(1)	114.9(2)
C(4)-C(3)-H(7)	108.5
N(1)-C(3)-H(7)	108.5
C(4)-C(3)-H(6)	108.5
N(1)-C(3)-H(6)	108.5
H(7)-C(3)-H(6)	107.5
C(3)-C(4)-C(5)	109.8(2)
C(3)-C(4)-H(9)	109.7
C(5)-C(4)-H(9)	109.7
C(3)-C(4)-H(8)	109.7
C(5)-C(4)-H(8)	109.7
H(9)-C(4)-H(8)	108.2
C(5)#1-C(5)-C(4)	112.7(3)
C(5)#1-C(5)-H(11)	109.0
C(4)-C(5)-H(11)	109.0
C(5)#1-C(5)-H(10)	109.0
C(4)-C(5)-H(10)	109.0
H(11)-C(5)-H(10)	107.8
N(2)-C(6)-C(6)#2	109.4(3)
N(2)-C(6)-H(18)	109.8
C(6)#2-C(6)-H(18)	109.8
N(2)-C(6)-H(17)	109.8
C(6)#2-C(6)-H(17)	109.8
H(18)-C(6)-H(17)	108.2
C(1)-N(1)-C(2)	113.2(2)
C(1)-N(1)-C(3)	113.1(2)
C(2)-N(1)-C(3)	111.5(2)
C(1)-N(1)-H(5)	107(2)
C(2)-N(1)-H(5)	107(2)
C(3)-N(1)-H(5)	104(2)

C(6)-N(2)-H(15)	109.5
C(6)-N(2)-H(16)	109.5
H(15)-N(2)-H(16)	109.5
C(6)-N(2)-H(14)	109.5
H(15)-N(2)-H(14)	109.5
H(16)-N(2)-H(14)	109.5
P(1)-O(1)-H(12)	109.5
P(2)-O(5)-H(13)	109.5
H(20)-O(7)-H(19)	106(6)
O(3)-P(1)-O(2)	118.24(15)
O(3)-P(1)-O(1)	111.15(14)
O(2)-P(1)-O(1)	109.71(15)
O(3)-P(1)-C(1)	111.02(15)
O(2)-P(1)-C(1)	103.54(14)
O(1)-P(1)-C(1)	101.68(13)
O(4)-P(2)-O(6)	120.82(16)
O(4)-P(2)-O(5)	106.58(14)
O(6)-P(2)-O(5)	110.12(13)
O(4)-P(2)-C(2)	108.03(14)
O(6)-P(2)-C(2)	104.70(14)
O(5)-P(2)-C(2)	105.65(15)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3,-y,-z #2 -x+1,-y+1,-z+1

Table 8.1.4. Anisotropic displacement parameters (A^2 x 10^3) for (en)(HDTMP). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	23(1)	20(1)	32(2)	-2(1)	-1(1)	-9(1)
C(2)	28(2)	24(2)	36(2)	4(1)	3(1)	-7(1)
C(3)	24(1)	26(2)	30(2)	-2(1)	4(1)	-13(1)
C(4)	31(2)	35(2)	28(2)	-4(1)	3(1)	-16(1)
C(5)	30(2)	32(2)	31(2)	-4(1)	5(1)	-14(1)
C(6)	33(2)	30(2)	32(2)	0(1)	2(1)	-10(1)
N(1)	24(1)	20(1)	24(1)	-3(1)	3(1)	-9(1)
N(2)	32(1)	37(2)	27(1)	-3(1)	1(1)	-15(1)
O(1)	27(1)	36(1)	41(1)	-3(1)	-1(1)	-5(1)
O(2)	55(2)	28(1)	42(1)	-8(1)	-15(1)	-11(1)
O(3)	44(1)	42(1)	38(1)	8(1)	-2(1)	-23(1)
O(4)	52(2)	45(2)	44(2)	-21(1)	15(1)	-30(1)
O(5)	33(1)	23(1)	47(1)	-2(1)	-12(1)	-12(1)
O(6)	43(1)	44(1)	33(1)	13(1)	-13(1)	-26(1)
O(7)	44(2)	58(2)	50(2)	3(2)	-9(1)	-30(1)
O(8)	56(2)	79(2)	78(2)	-32(2)	4(2)	-21(2)
P(1)	27(1)	20(1)	29(1)	-2(1)	-3(1)	-8(1)
P(2)	30(1)	28(1)	25(1)	-1(1)	0(1)	-17(1)

Table 8.1.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for (en)(HDTMP).

	x	y	z	U(eq)
H(1)	6919	1548	2282	30
H(2)	8188	1440	1386	30
H(3)	12383	-1368	2960	37
H(4)	11034	-1756	2254	37
H(7)	12109	2618	1639	31
H(6)	13781	624	2028	31
H(9)	11269	1173	568	36
H(8)	12598	-897	994	36
H(11)	14866	1666	384	37
H(10)	16157	-448	765	37
H(18)	4219	3447	5169	39
H(17)	5225	4260	5852	39
H(15)	2137	7080	5732	47
H(16)	1185	5569	5873	47
H(14)	1270	6483	5032	47
H(12)	3727	5365	1398	55
H(13)	7200	-2596	2881	50
H(5)	10270(60)	1840(50)	2750(20)	28(9)
H(20)	260(110)	5940(80)	740(40)	80(17)
H(19)	2140(130)	5550(110)	200(50)	110(30)

8.2. {Sr[(HDTMP)(H_2O)$_6$]·2H_2O} (Sr-HDTMP, 1)

Table 8.2.1. Crystal data and structure refinement for Sr-HDTMP

	Sr-HDTMP
Empirical formula	$C_{10}H_{42}N_2O_{20}P_4Sr$
Formula weight	721.96
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c (No.15)
Unit cell dimensions	
a (Å)	13.999(4)
b (Å)	5.9939 (13)
c (Å)	33.447 (12)
α (deg)	90
β (deg)	101.52(2)
γ (deg)	90
Volume (Å^3)	2750.1 (14)
Z	4
Density (calc.) (Mg m^{-3})	1.744
Absorption coefficient (mm^{-1})	2.279
F(000)	1496
Crystal size (mm)	0.26 x 0.238 x 0.04
θ range for data collection (deg)	2.97 to 23.29
Index ranges	$-10 \le h \le 15$, $-6 \le k \le 6$, $-37 \le l \le 37$
Reflections collected	6177
Independent reflections	1992 [R(int) = 0.0255]
Independent reflections [$I > 2\sigma(I)$]	1936[R(int) = 0.0177]
Max. and min. transmission	
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1992 / 0 / 182
Goodness-of-fit on F^2	1.141
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0365, $wR2$ = 0.1032
R indices (all data)	$R1$ = 0.0375, $wR2$ = 0.1037
Largest diff. peak and hole (e Å^{-3})	0.592 and –0.545

Table 8.2.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Sr-HDTMP. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Sr(1)	10000	1217(1)	7500	25(1)
P(1)	10276(1)	2936(2)	5890(1)	22(1)
P(2)	7828(1)	3276(2)	6727(1)	23(1)
C(1)	8644(3)	-986(6)	5868(1)	23(1)
C(2)	7962(3)	-551(7)	5464(1)	28(1)
C(3)	7822(3)	-2676(7)	5211(1)	30(1)
C(4)	9062(3)	3061(6)	6008(1)	23(1)
C(5)	7826(3)	1148(7)	6341(1)	28(1)
N(1)	8736(2)	920(5)	6170(1)	20(1)
O(1)	10264(2)	1988(5)	5477(1)	36(1)
O(2)	10869(2)	1728(5)	6250(1)	35(1)
O(3)	10554(2)	5457(5)	5910(1)	31(1)
O(4)	6994(2)	2667(5)	6923(1)	35(1)
O(5)	7633(2)	5541(5)	6489(1)	34(1)
O(6)	8834(2)	3457(5)	6981(1)	36(1)
O(7)	9980(2)	-1552(5)	6819(1)	38(1)
O(8)	8536(3)	-1641(6)	7354(1)	54(1)
O(9)	11074(2)	3195(6)	7055(1)	49(1)
O(10)	772(2)	7809(5)	5305(1)	42(1)

Table 8.2.3. Bond lengths [A] and angles [deg] for Sr-HDTMP.

Sr(1)-O(6)#1	2.519(3)
Sr(1)-O(6)	2.519(3)
Sr(1)-O(9)#1	2.603(3)
Sr(1)-O(9)	2.603(3)
Sr(1)-O(8)	2.641(3)
Sr(1)-O(8)#1	2.641(3)
Sr(1)-O(7)	2.814(3)
Sr(1)-O(7)#1	2.814(3)
P(1)-O(1)	1.490(3)
P(1)-O(2)	1.505(3)
P(1)-O(3)	1.558(3)
P(1)-C(4)	1.820(4)
P(2)-O(4)	1.494(3)
P(2)-O(6)	1.497(3)
P(2)-O(5)	1.570(3)
P(2)-C(5)	1.815(4)
C(1)-N(1)	1.513(5)
C(1)-C(2)	1.513(5)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-C(3)	1.521(6)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(3)#2	1.528(7)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-N(1)	1.500(5)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-N(1)	1.503(5)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
N(1)-H(1)	0.74(4)
O(3)-H(2)	0.73(5)
O(5)-H(3)	0.81(7)
O(6)#1-Sr(1)-O(6)	115.59(14)
O(6)#1-Sr(1)-O(9)#1	74.47(11)
O(6)-Sr(1)-O(9)#1	77.42(10)
O(6)#1-Sr(1)-O(9)	77.42(10)
O(6)-Sr(1)-O(9)	74.47(11)
O(9)#1-Sr(1)-O(9)	125.81(17)
O(6)#1-Sr(1)-O(8)	147.72(10)
O(6)-Sr(1)-O(8)	81.14(11)
O(9)#1-Sr(1)-O(8)	83.44(12)
O(9)-Sr(1)-O(8)	134.84(10)
O(6)#1-Sr(1)-O(8)#1	81.14(11)
O(6)-Sr(1)-O(8)#1	147.72(10)
O(9)#1-Sr(1)-O(8)#1	134.84(10)
O(9)-Sr(1)-O(8)#1	83.44(12)
O(8)-Sr(1)-O(8)#1	99.11(18)
O(6)#1-Sr(1)-O(7)	140.56(9)
O(6)-Sr(1)-O(7)	81.75(9)
O(9)#1-Sr(1)-O(7)	144.88(10)
O(9)-Sr(1)-O(7)	73.70(10)
O(8)-Sr(1)-O(7)	65.51(10)
O(8)#1-Sr(1)-O(7)	69.47(10)
O(6)#1-Sr(1)-O(7)#1	81.75(9)
O(6)-Sr(1)-O(7)#1	140.56(9)

O(9)#1-Sr(1)-O(7)#1	73.70(10)
O(9)-Sr(1)-O(7)#1	144.88(10)
O(8)-Sr(1)-O(7)#1	69.47(10)
O(8)#1-Sr(1)-O(7)#1	65.51(10)
O(7)-Sr(1)-O(7)#1	107.71(13)
O(1)-P(1)-O(2)	117.39(18)
O(1)-P(1)-O(3)	111.43(18)
O(2)-P(1)-O(3)	109.84(18)
O(1)-P(1)-C(4)	112.19(17)
O(2)-P(1)-C(4)	103.70(16)
O(3)-P(1)-C(4)	100.77(16)
O(4)-P(2)-O(6)	119.92(17)
O(4)-P(2)-O(5)	111.20(17)
O(6)-P(2)-O(5)	105.88(18)
O(4)-P(2)-C(5)	104.49(18)
O(6)-P(2)-C(5)	108.79(18)
O(5)-P(2)-C(5)	105.74(18)
N(1)-C(1)-C(2)	114.9(3)
N(1)-C(1)-H(1A)	108.6
C(2)-C(1)-H(1A)	108.6
N(1)-C(1)-H(1B)	108.6
C(2)-C(1)-H(1B)	108.6
H(1A)-C(1)-H(1B)	107.5
C(1)-C(2)-C(3)	110.0(3)
C(1)-C(2)-H(2A)	109.7
C(3)-C(2)-H(2A)	109.7
C(1)-C(2)-H(2B)	109.7
C(3)-C(2)-H(2B)	109.7
H(2A)-C(2)-H(2B)	108.2
C(2)-C(3)-C(3)#2	112.7(4)
C(2)-C(3)-H(3A)	109.1
C(3)#2-C(3)-H(3A)	109.1
C(2)-C(3)-H(3B)	109.1
C(3)#2-C(3)-H(3B)	109.1
H(3A)-C(3)-H(3B)	107.8
N(1)-C(4)-P(1)	114.1(2)
N(1)-C(4)-H(4A)	108.7
P(1)-C(4)-H(4A)	108.7
N(1)-C(4)-H(4B)	108.7
P(1)-C(4)-H(4B)	108.7
H(4A)-C(4)-H(4B)	107.6
N(1)-C(5)-P(2)	117.0(3)
N(1)-C(5)-H(5A)	108.0
P(2)-C(5)-H(5A)	108.0
N(1)-C(5)-H(5B)	108.0
P(2)-C(5)-H(5B)	108.0
H(5A)-C(5)-H(5B)	107.3
C(4)-N(1)-C(5)	113.7(3)
C(4)-N(1)-C(1)	113.3(3)
C(5)-N(1)-C(1)	111.0(3)
C(4)-N(1)-H(1)	104(3)
C(5)-N(1)-H(1)	110(3)
C(1)-N(1)-H(1)	104(3)
P(1)-O(3)-H(2)	116(4)
P(2)-O(5)-H(3)	117(5)
P(2)-O(6)-Sr(1)	139.39(18)

Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y,-z+3/2 #2 -x+3/2,-y-1/2,-z+1

Table 8.2.4. Anisotropic displacement parameters (A^2 x 10^3) for Sr-HDTMP. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Sr(1)	23(1)	32(1)	19(1)	0	0(1)	0
P(1)	19(1)	25(1)	22(1)	1(1)	5(1)	2(1)
P(2)	22(1)	26(1)	21(1)	-1(1)	5(1)	4(1)
C(1)	26(2)	21(2)	22(2)	-6(2)	4(2)	0(2)
C(2)	31(2)	29(2)	22(2)	-3(2)	0(2)	1(2)
C(3)	32(2)	32(2)	24(2)	-3(2)	-1(2)	0(2)
C(4)	23(2)	20(2)	25(2)	1(2)	5(2)	1(2)
C(5)	26(2)	30(2)	28(2)	-9(2)	11(2)	-6(2)
N(1)	18(2)	23(2)	17(2)	-2(1)	0(1)	1(1)
O(1)	44(2)	36(2)	31(2)	-4(1)	15(1)	3(1)
O(2)	25(1)	45(2)	32(2)	10(1)	3(1)	7(1)
O(3)	33(2)	29(2)	34(2)	-1(1)	9(1)	-9(1)
O(4)	33(2)	41(2)	33(2)	1(1)	16(1)	4(1)
O(5)	27(2)	30(2)	47(2)	9(1)	8(1)	6(1)
O(6)	28(2)	48(2)	27(2)	-2(1)	-2(1)	2(1)
O(7)	34(2)	46(2)	32(2)	4(1)	4(1)	8(1)
O(8)	56(2)	69(2)	37(2)	-2(2)	8(2)	-28(2)
O(9)	48(2)	61(2)	39(2)	-5(2)	14(2)	-16(2)
O(10)	54(2)	33(2)	40(2)	8(1)	14(2)	7(1)

Table 8.2.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Sr-HDTMP.

	x	y	z	U(eq)
H(1A)	8418	-2296	5992	28
H(1B)	9286	-1322	5816	28
H(2A)	8231	607	5317	34
H(2B)	7337	-40	5512	34
H(3A)	7529	-3806	5355	51(15)
H(3B)	8454	-3223	5178	64(17)
H(4A)	9052	4230	6207	27
H(4B)	8600	3467	5762	27
H(5A)	7698	-279	6457	33
H(5B)	7287	1451	6116	33
H(1)	9150(30)	590(70)	6333(13)	20(12)
H(2)	10580(40)	5990(90)	5714(16)	44(17)
H(3)	7080(50)	5760(120)	6360(20)	80(20)

8.3. {Ba[(HDTMP)(H_2O)$_6$]·2H_2O} (Ba-HDTMP, 2)

Table 8.3.1. Crystal data and structure refinement for Ba-HDTMP

	Ba-HDTMP
Empirical formula	$C_{10}H_{42}BaN_2O_{20}P_4$
Formula weight	771.68
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c (No.15)
Unit cell dimensions	
a (Å)	14.084(4)
b (Å)	6.0158(15)
c (Å)	33.793(9)
α (deg)	90
β (deg)	100.717(4)
γ (deg)	90
Volume (Å^3)	2813.3(12)
Z	4
Density (calc.) (Mg m^{-3})	1.822
Absorption coefficient (mm^{-1})	1.723
F(000)	1568
Crystal size (mm)	0.22 x 0.18 x 0.10
θ range for data collection (deg)	2.45 to 28.01
Index ranges	$-17 \le h \le 15$, $-7 \le k \le 7$, $-43 \le l \le 42$
Reflections collected	8568
Independent reflections	3086 [R(int) = 0.0383]
Independent reflections [$I > 2\sigma(I)$]	2982 [R(int) = 0.0257]
Max. and min. transmission	
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3086 / 0 / 175
Goodness-of-fit on F^2	1.281
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0345, $wR2$ = 0.0905
R indices (all data)	$R1$ = 0.0361, $wR2$ = 0.0913
Largest diff. peak and hole (e Å^{-3})	0.603 and –1.214

Table 8.3.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Ba-HDTMP. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Ba(1)	5000	1308(1)	2500	24(1)
C(1)	6375(2)	-981(5)	4146(1)	22(1)
C(2)	7045(2)	-542(6)	4544(1)	27(1)
C(3)	7181(3)	-2675(6)	4795(1)	29(1)
C(4)	7185(2)	1120(6)	3671(1)	28(1)
C(5)	5965(2)	3060(5)	4012(1)	21(1)
N(1)	6280(2)	925(4)	3848(1)	19(1)
O(1)	8051(2)	2724(5)	3108(1)	33(1)
O(2)	7436(2)	5519(4)	3562(1)	32(1)
O(3)	6235(2)	3627(5)	3054(1)	36(1)
O(4)	4183(2)	1700(5)	3773(1)	34(1)
O(5)	4464(2)	5455(4)	4101(1)	31(1)
O(6)	4751(2)	2013(5)	4537(1)	35(1)
O(7)	6507(3)	-1788(6)	2639(1)	56(1)
O(8)	5071(2)	-1596(5)	3212(1)	37(1)
O(9)	3908(3)	3407(6)	2989(1)	52(1)
O(10)	4231(2)	7819(5)	4696(1)	41(1)
P(1)	7221(1)	3335(1)	3307(1)	21(1)
P(2)	4752(1)	2938(1)	4127(1)	21(1)

Table 8.3.3. Bond lengths [A] and angles [deg] for Ba-HDTMP.

Ba(1)-O(3)	2.696(3)
Ba(1)-O(3)#1	2.696(3)
Ba(1)-O(9)#1	2.763(3)
Ba(1)-O(9)	2.763(3)
Ba(1)-O(7)#1	2.797(3)
Ba(1)-O(7)	2.797(3)
Ba(1)-O(8)#1	2.961(3)
Ba(1)-O(8)	2.961(3)
C(1)-C(2)	1.515(4)
C(1)-N(1)	1.517(4)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-C(3)	1.529(5)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(3)#2	1.521(6)
C(3)-H(3B)	0.9700
C(3)-H(3A)	0.9700
C(4)-N(1)	1.509(4)
C(4)-P(1)	1.822(3)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-N(1)	1.499(4)
C(5)-P(2)	1.822(3)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
N(1)-H(1C)	0.88(4)
O(1)-P(1)	1.497(3)
O(2)-P(1)	1.570(3)
O(2)-H(2C)	0.8200
O(3)-P(1)	1.499(3)
O(4)-P(2)	1.507(3)
O(5)-P(2)	1.566(3)
O(5)-H(5D)	0.8200
O(6)-P(2)	1.493(3)

O(3)-Ba(1)-O(3)#1	117.66(12)
O(3)-Ba(1)-O(9)#1	79.59(9)
O(3)#1-Ba(1)-O(9)#1	72.99(10)
O(3)-Ba(1)-O(9)	72.99(10)
O(3)#1-Ba(1)-O(9)	79.59(9)
O(9)#1-Ba(1)-O(9)	125.60(15)
O(3)-Ba(1)-O(7)#1	146.37(9)
O(3)#1-Ba(1)-O(7)#1	81.76(10)
O(9)#1-Ba(1)-O(7)#1	133.92(9)
O(9)-Ba(1)-O(7)#1	85.13(12)
O(3)-Ba(1)-O(7)	81.76(10)
O(3)#1-Ba(1)-O(7)	146.37(9)
O(9)#1-Ba(1)-O(7)	85.13(12)
O(9)-Ba(1)-O(7)	133.92(9)
O(7)#1-Ba(1)-O(7)	96.50(18)
O(3)-Ba(1)-O(8)#1	142.16(8)
O(3)#1-Ba(1)-O(8)#1	79.69(8)
O(9)#1-Ba(1)-O(8)#1	73.86(9)
O(9)-Ba(1)-O(8)#1	144.82(10)
O(7)#1-Ba(1)-O(8)#1	63.97(9)
O(7)-Ba(1)-O(8)#1	69.71(9)
O(3)-Ba(1)-O(8)	79.69(8)
O(3)#1-Ba(1)-O(8)	142.16(8)

O(9)#1-Ba(1)-O(8)	144.82(10)
O(9)-Ba(1)-O(8)	73.86(9)
O(7)#1-Ba(1)-O(8)	69.71(9)
O(7)-Ba(1)-O(8)	63.97(9)
O(8)#1-Ba(1)-O(8)	107.69(11)
C(2)-C(1)-N(1)	115.0(3)
C(2)-C(1)-H(1A)	108.5
N(1)-C(1)-H(1A)	108.5
C(2)-C(1)-H(1B)	108.5
N(1)-C(1)-H(1B)	108.5
H(1A)-C(1)-H(1B)	107.5
C(1)-C(2)-C(3)	109.8(3)
C(1)-C(2)-H(2A)	109.7
C(3)-C(2)-H(2A)	109.7
C(1)-C(2)-H(2B)	109.7
C(3)-C(2)-H(2B)	109.7
H(2A)-C(2)-H(2B)	108.2
C(3)#2-C(3)-C(2)	112.4(4)
C(3)#2-C(3)-H(3B)	109.1
C(2)-C(3)-H(3B)	109.1
C(3)#2-C(3)-H(3A)	109.1
C(2)-C(3)-H(3A)	109.1
H(3B)-C(3)-H(3A)	107.9
N(1)-C(4)-P(1)	117.2(2)
N(1)-C(4)-H(4A)	108.0
P(1)-C(4)-H(4A)	108.0
N(1)-C(4)-H(4B)	108.0
P(1)-C(4)-H(4B)	108.0
H(4A)-C(4)-H(4B)	107.2
N(1)-C(5)-P(2)	113.5(2)
N(1)-C(5)-H(5A)	108.9
P(2)-C(5)-H(5A)	108.9
N(1)-C(5)-H(5B)	108.9
P(2)-C(5)-H(5B)	108.9
H(5A)-C(5)-H(5B)	107.7
C(5)-N(1)-C(4)	114.2(2)
C(5)-N(1)-C(1)	113.4(2)
C(4)-N(1)-C(1)	110.2(2)
C(5)-N(1)-H(1C)	104(3)
C(4)-N(1)-H(1C)	110(3)
C(1)-N(1)-H(1C)	104(3)
P(1)-O(2)-H(2C)	109.5
P(1)-O(3)-Ba(1)	138.13(17)
P(2)-O(5)-H(5D)	109.5
O(1)-P(1)-O(3)	119.45(16)
O(1)-P(1)-O(2)	111.40(15)
O(3)-P(1)-O(2)	106.13(16)
O(1)-P(1)-C(4)	104.23(16)
O(3)-P(1)-C(4)	109.32(16)
O(2)-P(1)-C(4)	105.52(17)
O(6)-P(2)-O(4)	117.40(17)
O(6)-P(2)-O(5)	111.52(15)
O(4)-P(2)-O(5)	109.88(16)
O(6)-P(2)-C(5)	112.03(16)
O(4)-P(2)-C(5)	103.41(15)
O(5)-P(2)-C(5)	101.11(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2 #2 -x+3/2,-y-1/2,-z+1

Table 8.3.4. Anisotropic displacement parameters (A^2 x 10^3) for Ba-HDTMP. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ba(1)	24(1)	27(1)	18(1)	0	-1(1)	0
C(1)	25(1)	18(1)	21(1)	4(1)	3(1)	-2(1)
C(2)	29(2)	27(2)	22(2)	5(1)	-3(1)	-2(1)
C(3)	32(2)	31(2)	21(2)	7(1)	-1(1)	0(1)
C(4)	25(2)	28(2)	34(2)	10(1)	14(1)	7(1)
C(5)	20(1)	19(1)	23(1)	-1(1)	4(1)	-1(1)
N(1)	18(1)	18(1)	19(1)	2(1)	2(1)	0(1)
O(1)	34(1)	38(1)	31(1)	-4(1)	16(1)	-4(1)
O(2)	23(1)	29(1)	45(2)	-10(1)	9(1)	-7(1)
O(3)	30(1)	47(2)	28(1)	0(1)	-6(1)	-3(1)
O(4)	25(1)	41(2)	34(1)	-13(1)	1(1)	-7(1)
O(5)	32(1)	25(1)	37(1)	1(1)	9(1)	9(1)
O(6)	43(1)	35(1)	28(1)	4(1)	14(1)	-2(1)
O(7)	66(2)	66(2)	36(2)	4(2)	11(2)	33(2)
O(8)	36(1)	44(2)	30(1)	-2(1)	4(1)	-11(1)
O(9)	58(2)	59(2)	42(2)	6(2)	18(2)	21(2)
O(10)	54(2)	33(1)	37(2)	-7(1)	11(1)	-6(1)
P(1)	21(1)	22(1)	20(1)	0(1)	4(1)	-4(1)
P(2)	18(1)	23(1)	21(1)	-1(1)	4(1)	-2(1)

Table 8.3.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Ba-HDTMP.

	x	y	z	U(eq)
H(1A)	5738	-1331	4200	26
H(1B)	6606	-2279	4023	26
H(2A)	6774	609	4691	33
H(2B)	7666	-28	4495	33
H(3B)	6554	-3215	4831	45(13)
H(3A)	7470	-3803	4649	62(17)
H(4A)	7282	-282	3543	33
H(4B)	7727	1323	3891	33
H(5A)	5987	4234	3817	25
H(5B)	6418	3442	4255	25
H(1C)	5790(30)	550(70)	3659(12)	25(10)
H(2C)	8021	5667	3633	53(15)
H(5D)	4423	5909	4326	46

8.3. {Cu[(HDTMP)(H_2O)$_4$]·6H_2O} (Cu-HDTMP, 3)

Table 8.3.1. Crystal data and structure refinement for Cu-HDTMP.

	Cu-HDTMP
Empirical formula	$C_{10}H_{46}CuN_2O_{22}P_4$
Formula weight	733.91
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1 (No.2)
Unit cell dimensions	
a (Å)	6.267(2)
b (Å)	7.6810(12)
c (Å)	16.879(7)
α (deg)	86.36(3)
β (deg)	83.74(2)
γ (deg)	66.44(2)
Volume (Å^3)	740.1(4)
Z	1
Density (calc.) (Mg m^{-3})	1.647
Absorption coefficient (mm^{-1})	1.043
F(000)	385
Crystal size (mm)	0.18 x 0.08 x 0.05
θ range for data collection (deg)	2.43 to 26.00
Index ranges	$-7 \le h \le 6$, $-9 \le k \le 9$, $-20 \le l \le 20$
Reflections collected	4540
Independent reflections	2857 [R(int) = 0.0147]
Independent reflections [$I > 2\sigma(I)$]	2457 [R(int) = 0.0242]
Max. and min. transmission	
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2857 / 0 / 230
Goodness-of-fit on F^2	1.033
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0324, $wR2$ = 0.0848
R indices (all data)	$R1$ = 0.0399, $wR2$ = 0.0876
Largest diff. peak and hole (e Å^{-3})	0.316 and –0.323

Table 8.3.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Cu-HDTMP. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cu(1)	5000	0	5000	26(1)
C(1)	3461(5)	-968(3)	2542(2)	29(1)
C(2)	4047(4)	1876(3)	1938(1)	24(1)
C(3)	513(4)	1264(3)	1696(1)	25(1)
C(4)	1509(4)	369(4)	889(1)	32(1)
C(5)	-443(4)	406(4)	414(1)	33(1)
N(1)	2327(3)	1059(3)	2262(1)	21(1)
O(1)	5967(3)	-3474(2)	3584(1)	29(1)
O(2)	7907(3)	-1552(2)	2759(1)	37(1)
O(3)	4795(3)	46(2)	3839(1)	33(1)
O(4)	1009(3)	5251(2)	2403(1)	37(1)
O(5)	1854(3)	4837(3)	900(1)	36(1)
O(6)	4931(3)	4911(3)	1747(1)	36(1)
O(7)	5022(4)	2556(3)	4865(1)	34(1)
O(8)	2356(4)	5361(3)	3917(1)	44(1)
O(9)	7137(4)	6150(4)	658(1)	46(1)
O(10)	8978(7)	2649(4)	3512(2)	65(1)
P(1)	5648(1)	-1535(1)	3251(1)	23(1)
P(2)	2758(1)	4421(1)	1703(1)	24(1)
O(11)	9249(4)	-1524(4)	4906(2)	56(1)

Table 8.3.3. Bond lengths [A] and angles [deg] for Cu-HDTMP.

Cu(1)-O(7)	1.9672(19)
Cu(1)-O(7)#1	1.9672(19)
Cu(1)-O(3)	1.9757(17)
Cu(1)-O(3)#1	1.9757(17)
Cu(1)-O(11)	2.434(3)
Cu(1)-O(11)#1	2.434(3)
C(1)-N(1)	1.500(3)
C(1)-P(1)	1.821(2)
C(1)-H(1A)	0.90(3)
C(1)-H(1B)	0.90(3)
C(2)-N(1)	1.492(3)
C(2)-P(2)	1.827(2)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-N(1)	1.518(3)
C(3)-C(4)	1.519(3)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.525(3)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(5)#2	1.520(5)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
N(1)-H(1C)	0.79(3)
O(1)-P(1)	1.5015(17)
O(2)-P(1)	1.5566(19)
O(2)-H(2C)	0.8200
O(3)-P(1)	1.5042(18)
O(4)-P(2)	1.5028(19)
O(5)-P(2)	1.4931(18)
O(6)-P(2)	1.5612(18)
O(6)-H(6A)	0.8200
O(7)-H(7A)	0.75(3)
O(7)-H(7B)	0.78(4)
O(8)-H(8A)	0.69(4)
O(8)-H(8B)	1.18(9)
O(9)-H(9A)	0.89(5)
O(9)-H(9B)	0.72(3)
O(10)-H(10B)	0.74(3)
O(10)-H(10A)	0.74(7)
O(11)-H(11A)	0.92(5)
O(11)-H(11B)	0.74(3)

O(7)-Cu(1)-O(7)#1	180.0
O(7)-Cu(1)-O(3)	87.49(8)
O(7)#1-Cu(1)-O(3)	92.51(8)
O(7)-Cu(1)-O(3)#1	92.51(8)
O(7)#1-Cu(1)-O(3)#1	87.49(8)
O(3)-Cu(1)-O(3)#1	180.0
O(7)-Cu(1)-O(11)	92.52(10)
O(7)#1-Cu(1)-O(11)	87.48(10)
O(3)-Cu(1)-O(11)	94.73(9)
O(3)#1-Cu(1)-O(11)	85.27(9)
O(7)-Cu(1)-O(11)#1	87.48(10)
O(7)#1-Cu(1)-O(11)#1	92.52(10)
O(3)-Cu(1)-O(11)#1	85.27(9)
O(3)#1-Cu(1)-O(11)#1	94.73(9)
O(11)-Cu(1)-O(11)#1	180.0

N(1)-C(1)-P(1)	117.80(16)
N(1)-C(1)-H(1A)	109.5(17)
P(1)-C(1)-H(1A)	108.5(17)
N(1)-C(1)-H(1B)	104.1(19)
P(1)-C(1)-H(1B)	106.0(19)
H(1A)-C(1)-H(1B)	111(3)
N(1)-C(2)-P(2)	114.49(15)
N(1)-C(2)-H(2A)	108.6
P(2)-C(2)-H(2A)	108.6
N(1)-C(2)-H(2B)	108.6
P(2)-C(2)-H(2B)	108.6
H(2A)-C(2)-H(2B)	107.6
N(1)-C(3)-C(4)	114.82(19)
N(1)-C(3)-H(3A)	108.6
C(4)-C(3)-H(3A)	108.6
N(1)-C(3)-H(3B)	108.6
C(4)-C(3)-H(3B)	108.6
H(3A)-C(3)-H(3B)	107.5
C(3)-C(4)-C(5)	110.6(2)
C(3)-C(4)-H(4A)	109.5
C(5)-C(4)-H(4A)	109.5
C(3)-C(4)-H(4B)	109.5
C(5)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	108.1
C(5)#2-C(5)-C(4)	112.9(3)
C(5)#2-C(5)-H(5A)	109.0
C(4)-C(5)-H(5A)	109.0
C(5)#2-C(5)-H(5B)	109.0
C(4)-C(5)-H(5B)	109.0
H(5A)-C(5)-H(5B)	107.8
C(2)-N(1)-C(1)	113.05(18)
C(2)-N(1)-C(3)	113.67(17)
C(1)-N(1)-C(3)	110.21(17)
C(2)-N(1)-H(1C)	108.8(19)
C(1)-N(1)-H(1C)	105.4(19)
C(3)-N(1)-H(1C)	105.1(19)
P(1)-O(2)-H(2C)	109.5
P(1)-O(3)-Cu(1)	131.02(10)
P(2)-O(6)-H(6A)	109.5
Cu(1)-O(7)-H(7A)	109(2)
Cu(1)-O(7)-H(7B)	114(3)
H(7A)-O(7)-H(7B)	111(4)
H(8A)-O(8)-H(8B)	114(5)
H(9A)-O(9)-H(9B)	112(4)
H(10B)-O(10)-H(10A)	82(6)
O(1)-P(1)-O(3)	116.40(10)
O(1)-P(1)-O(2)	111.62(10)
O(3)-P(1)-O(2)	109.18(11)
O(1)-P(1)-C(1)	105.41(11)
O(3)-P(1)-C(1)	107.56(11)
O(2)-P(1)-C(1)	106.01(12)
O(5)-P(2)-O(4)	116.56(11)
O(5)-P(2)-O(6)	112.70(10)
O(4)-P(2)-O(6)	109.55(11)
O(5)-P(2)-C(2)	112.47(11)
O(4)-P(2)-C(2)	104.22(11)
O(6)-P(2)-C(2)	99.74(10)
Cu(1)-O(11)-H(11A)	121(3)
Cu(1)-O(11)-H(11B)	82(3)
H(11A)-O(11)-H(11B)	85(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1 #2 -x,-y,-z

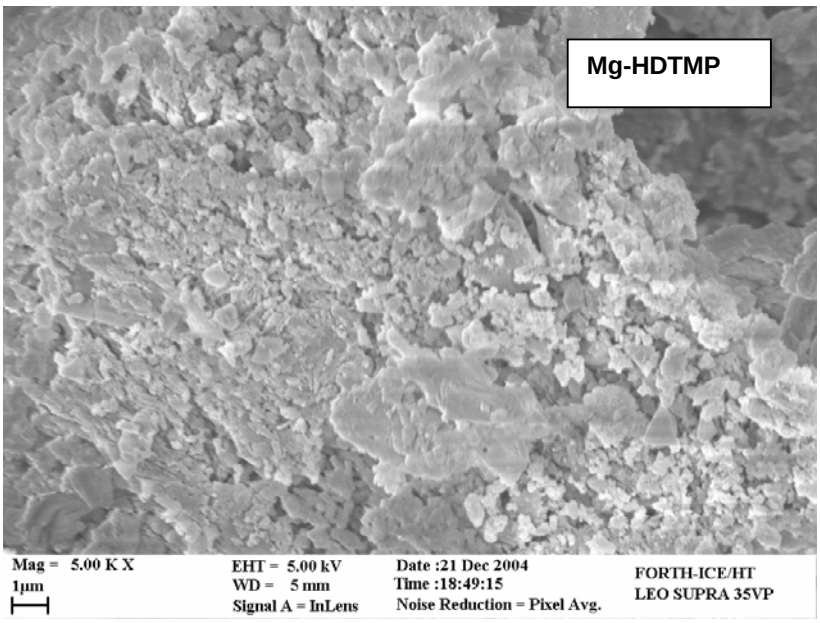
Table 8.3.4. Anisotropic displacement parameters (A^2 x 10^3) for Cu-HDTMP. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

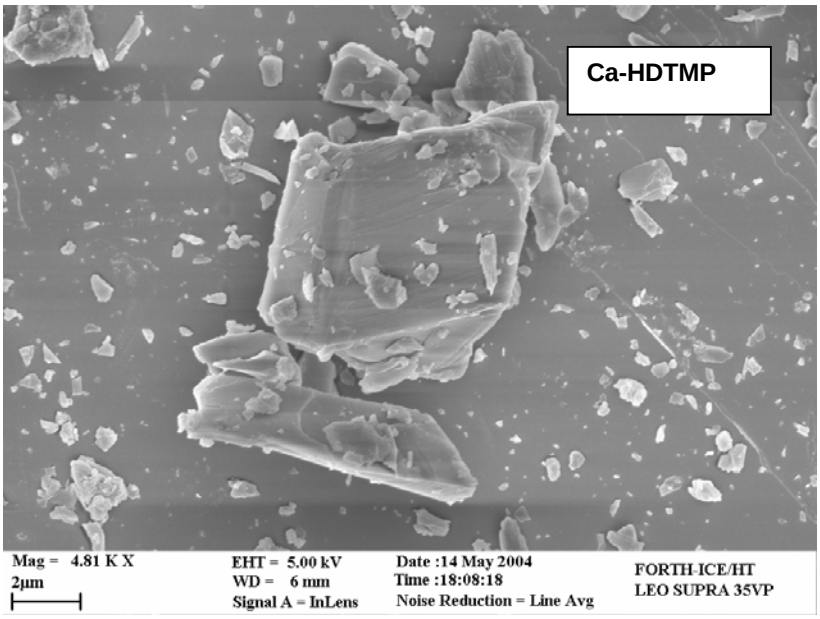
	U11	U22	U33	U23	U13	U12
Cu(1)	34(1)	23(1)	21(1)	0(1)	-5(1)	-11(1)
C(1)	35(1)	22(1)	31(1)	4(1)	-12(1)	-12(1)
C(2)	21(1)	20(1)	29(1)	1(1)	-4(1)	-6(1)
C(3)	22(1)	28(1)	27(1)	1(1)	-8(1)	-9(1)
C(4)	30(1)	38(1)	28(1)	-5(1)	-8(1)	-12(1)
C(5)	30(1)	41(1)	29(1)	-6(1)	-9(1)	-13(1)
N(1)	21(1)	20(1)	21(1)	-3(1)	-4(1)	-6(1)
O(1)	33(1)	22(1)	29(1)	2(1)	-5(1)	-7(1)
O(2)	25(1)	24(1)	53(1)	3(1)	4(1)	-4(1)
O(3)	45(1)	25(1)	23(1)	-2(1)	-8(1)	-7(1)
O(4)	35(1)	30(1)	35(1)	-5(1)	4(1)	-3(1)
O(5)	37(1)	41(1)	31(1)	8(1)	-12(1)	-14(1)
O(6)	40(1)	38(1)	40(1)	6(1)	-11(1)	-24(1)
O(7)	50(1)	30(1)	26(1)	1(1)	-8(1)	-18(1)
O(8)	50(1)	45(1)	39(1)	1(1)	-13(1)	-19(1)
O(9)	37(1)	67(2)	36(1)	2(1)	-2(1)	-22(1)
O(10)	66(2)	46(2)	53(2)	1(1)	14(1)	3(2)
P(1)	24(1)	20(1)	22(1)	0(1)	-5(1)	-5(1)
P(2)	24(1)	21(1)	25(1)	0(1)	-4(1)	-6(1)
O(11)	40(1)	59(2)	63(2)	-13(2)	0(1)	-12(1)

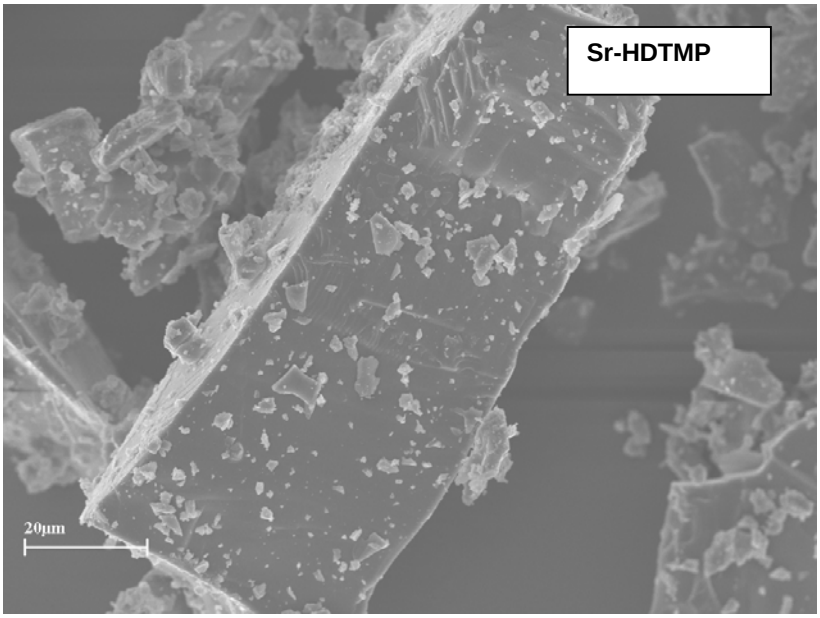
Table 8.3.5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Cu-HDTMP.

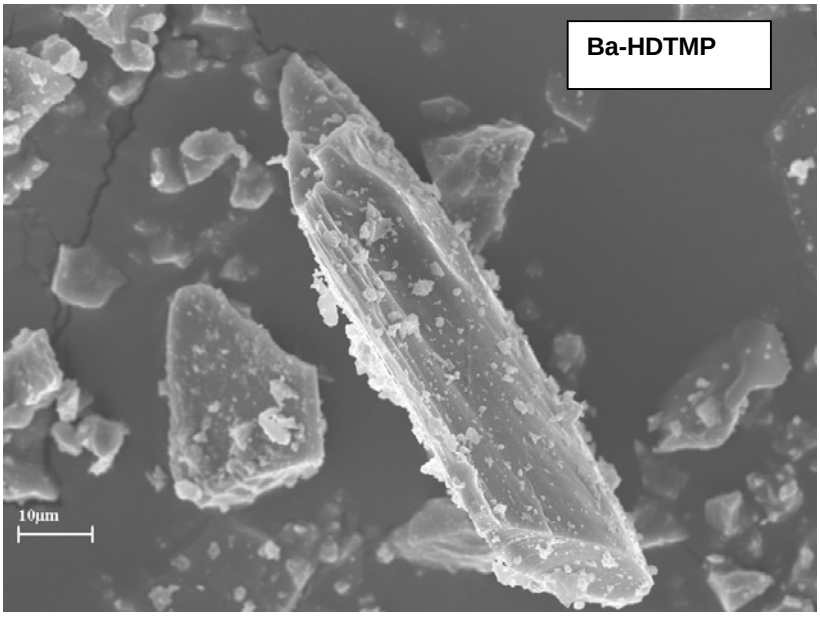
	x	y	z	U(eq)
H(2A)	4891	1210	1458	29
H(2B)	5173	1648	2325	29
H(3A)	-417	2606	1612	31
H(3B)	-526	694	1948	31
H(4A)	2600	-934	964	38
H(4B)	2353	1059	595	38
H(5A)	-1249	-318	704	40
H(5B)	-1564	1707	363	40
H(2C)	8810	-2653	2671	55
H(6A)	5293	5283	1307	54
H(1A)	4100(50)	-1720(40)	2116(17)	33(7)
H(1C)	1600(50)	1630(40)	2644(17)	26(7)
H(1B)	2280(50)	-1220(40)	2799(18)	40(8)
H(9A)	8560(90)	5720(60)	830(30)	93(15)
H(9B)	7180(60)	5860(50)	250(20)	40(10)
H(8A)	1910(70)	5060(60)	3620(30)	70(14)
H(10B)	9910(50)	2990(50)	3543(19)	22(10)
H(7A)	4710(60)	3020(40)	5260(20)	42(9)
H(7B)	4200(60)	3200(50)	4550(20)	54(11)
H(11A)	10050(80)	-2480(70)	4550(30)	85(14)
H(10A)	8250(120)	3680(100)	3500(40)	160(30)
H(11B)	9130(60)	-870(50)	4550(20)	39(11)
H(8B)	3910(150)	5820(120)	3680(50)	230(40)

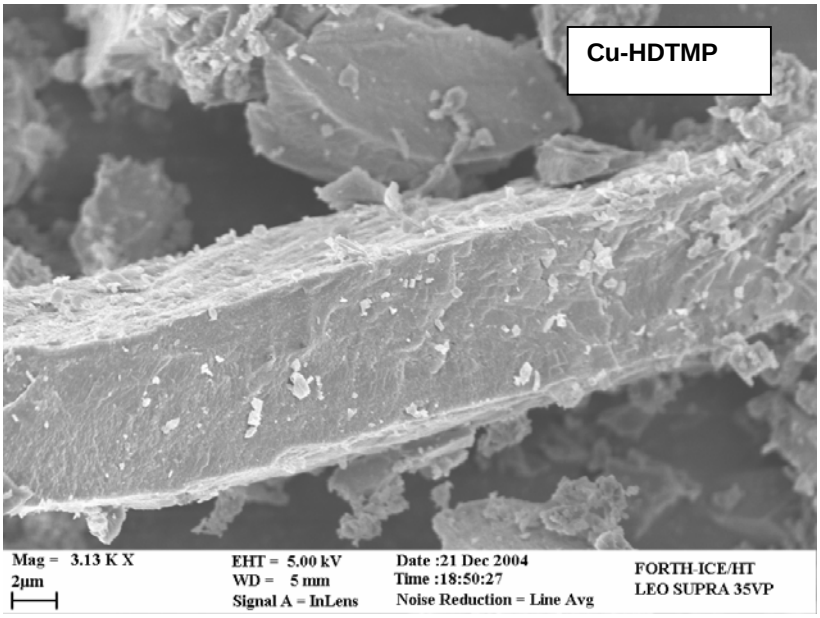
9. Scanning Electron Microscopy of Metal Phosphonate Compounds






Sr-HDTMP
20µm


Ba-HDTMP
10µm


Cu-HDTMP
Mag = 3.13 K X
2µm
EHT = 5.00 kV
WD = 5 mm
Signal A = InLens
Date :21 Dec 2004
Time :18:50:27
Noise Reduction = Line Avg
FORTH-ICE/HT
LEO SUPRA 35VP