

Supplementary Information (ESI) for the paper

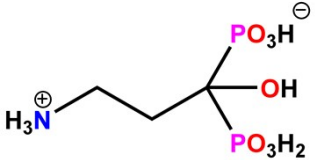
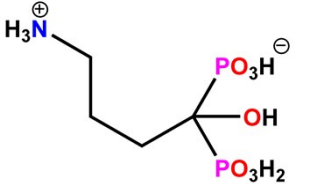
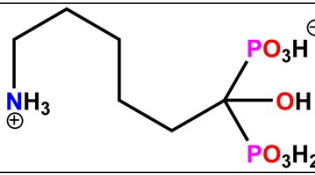
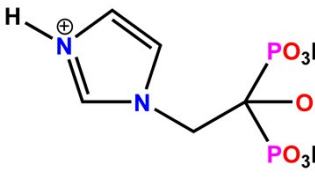
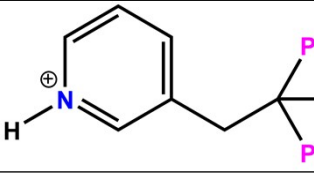
Deciphering preferred solid-state conformations in nitrogen-containing bisphosphonates and their coordination compounds. A case study of discrete Cu(II) complexes based on C_α-substituted analogues of zoledronic acid: crystal structures and solid state characterization

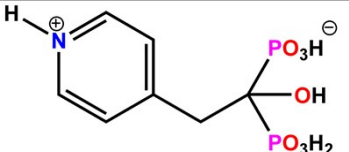
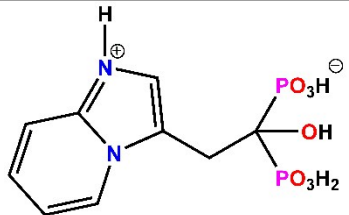
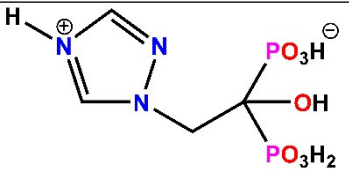
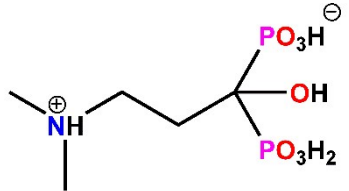
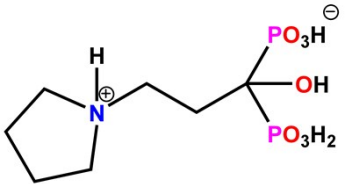
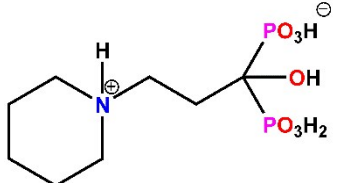
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Table S1. The list of crystal structures based on selected bisphosphonate ligands with the recognition of their conformation around C_α-C bond.

Lp.	Database refcode	Formula ^a	Space group	Dimensionality	Ligand conformation ^b		Source	
					I	II		
Ligands								
1.	SOPSEV		H ₄ Pam	P2 ₁	-	✓	✗	L. M. Shkol'nikova <i>et al.</i> , <i>Kristallografiya</i> , 35 (1990) 1442
2.	GOWZEX		H ₄ Ale	P2 ₁ /n	-	✓	✗	J. Ohanessian <i>et al.</i> , <i>Phosphorus, Sulfur Silicon Relat. Elem.</i> , 129 (1997) 99-110
	KOJGUL		H ₄ Ale·H ₂ O	P2 ₁ /n	-	✓	✗	Y. Leroux <i>et al.</i> , <i>Phosphorus, Sulfur Silicon Relat. Elem.</i> , 63 (1991) 181-191
3.	VUYTUE		H ₄ Ner	P2 ₁ /c	-	✓	✗	V. M. Coiro <i>et al.</i> , <i>Acta Cryst.</i> , C45 (1989) 446-448
4.	MEYGII		H ₄ Zol	P $\bar{1}$	-	✓	✗	V. V. Chernyshev <i>et al.</i> , <i>Acta Cryst.</i> , C69 (2013) 263-266
	BEKBOJ		H ₄ Zol·H ₂ O	P $\bar{1}$	-	✓	✗	J. M. Sanders <i>et al.</i> , <i>J. Med. Chem.</i> , 46 (2003) 5171-5183
	ORUZEH		H ₄ Zol·3H ₂ O	P $\bar{1}$	-	✓	✗	R. Ruscica <i>et al.</i> , <i>J. Pharm. Sci.</i> , 99 (2010) 4962-4972
5.	MOFVOS		H ₄ Ris·H ₂ O	P2 ₁ /n	-	✓	✗	C. Barbey <i>et al.</i> , <i>Z. Kristallogr. - New Cryst. Struct.</i> , 217 (2002) 137-138

6.	UPAVUD		H ₄ 4py-Ris	$P2_1/n$	-	✓	✗	F.-L. Wang <i>et al.</i> , <i>Acta Cryst.</i> , E67 (2011) o1025
7.	BIZWAI02		H ₄ Min·H ₂ O	$P\bar{1}$	-	✓	✗	A. Airoldi <i>et al.</i> , <i>Acta Cryst.</i> , E71 (2015) 51-54
8.	WETQES		H ₄ Tra	$P2_1/c$	-	✓	✗	J. Mao <i>et al.</i> , <i>J. Am. Chem. Soc.</i> , 128 (2006) 14485-14497
9.	FURCAW		H ₄ Olp·H ₂ O	$P2_1/n$	-	✗	✓	L. M. Shkol'nikova <i>et al.</i> , <i>Izv. Akad. Nauk SSSR, Ser. Khim.</i> , 36 (1987) 1394-1399
10.	GADPAD		H ₄ Prp	$P2_1/n$	-	✗	✓	D. Fernandez <i>et al.</i> , <i>Acta Cryst.</i> , C59 (2003) o228-o230
11.	EMIGIQ		H ₄ Ppp	$P2_1/c$	-	✓	✗	D. Fernandez <i>et al.</i> , <i>Acta Cryst.</i> , C59 (2003) o661-o663

1. H ₄ Pam							
1.	FENREW	Na(H ₃ Pam)·5H ₂ O	<i>P</i> $\bar{1}$	org.-inorg. salt	✓	✗	K. Stahl <i>et al.</i> , <i>Acta Cryst.</i> , E 61 (2005) m132-m134
2.	EFAMIH	Na ₂ (H ₂ Pam)·5H ₂ O	<i>P</i> $\bar{1}$	org.-inorg. salt	✓	✗	D. Vega <i>et al.</i> , <i>Acta Cryst.</i> , C 58 (2002) m77-m80
3.	IDAWIV	[Co(H ₃ Pam) ₂ (H ₂ O) ₂]	<i>P2</i> ₁ / <i>c</i>	0D	✓	✗	N. V. Tsaryk <i>et al.</i> , <i>Acta Cryst.</i> , E 67 (2011) m1694
4.	INIYUZ	[Zn(H ₃ Pam) ₂ (H ₂ O) ₂]	<i>P2</i> ₁ / <i>n</i>	0D	✓	✗	D. Fernandez <i>et al.</i> , <i>Acta Cryst.</i> , C 60 (2004) m73-m75
5.	FAZVUZ	[Ni(H ₃ Pam) ₂ (H ₂ O) ₂]	<i>P2</i> ₁ / <i>n</i>	0D	✓	✗	B. Demoro <i>et al.</i> , <i>Dalton Trans.</i> , 41 (2012) 6468-6476
6.	XEHTOU	[Ni ₂ (H ₃ Pam) ₄ (H ₂ O) ₂]·2H ₂ O	<i>P2</i> ₁ / <i>c</i>	0D	✓	✓	Y. Gong <i>et al.</i> , <i>Inorg. Chem.</i> , 45 (2006) 4987-4995
7.	DILTID	[Cu(2,2'-bpy)(H ₃ Pam)(Cl)(H ₂ O)]·2H ₂ O	<i>P</i> $\bar{1}$	0D	✓	✗	K. D. Demadis <i>et al.</i> , <i>Cryst. Growth Des.</i> , 13 (2013) 4480-4489
8.	KEVVOX01	[Cu(H ₂ Pam)]·H ₂ O	<i>P2</i> ₁ / <i>c</i>	1D	✓	✗	G. Li <i>et al.</i> , <i>J. Coord. Chem.</i> , 61 (2008) 540-549
9.	TAMMAX	[Ca(H ₂ Pam)(H ₂ O)]·H ₂ O	<i>Pna2</i> ₁	1D	✓	✗	D. Liu <i>et al.</i> , <i>Chem. Commun.</i> , 48 (2012) 2668-2670
10.	XEHTAG	[Mn(H ₂ Pam)]·H ₂ O	<i>P</i> $\bar{1}$	1D	✓	✗	Y. Gong <i>et al.</i> , <i>Inorg. Chem.</i> , 45 (2006) 4987-4995
11.	XEHTEK	[Co(H ₂ Pam)]·H ₂ O	<i>P</i> $\bar{1}$	1D	✓	✗	Y. Gong <i>et al.</i> , <i>Inorg. Chem.</i> , 45 (2006) 4987-4995
12.	BACMUP ^c	[Zn(H ₃ Pam) ₂]	<i>C2</i> / <i>c</i>	2D	✓	✗	H. A. Habib <i>et al.</i> , <i>Polyhedron</i> , 29 (2010) 2537-2545
13.	XEHTUA	[Zn(H ₂ Pam)]·H ₂ O	<i>P2</i> ₁ / <i>c</i>	2D	✗	✓	Y. Gong <i>et al.</i> , <i>Inorg. Chem.</i> , 45 (2006) 4987-4995
14.	XEHTIO	[Cu ₃ (HPam) ₂ (H ₂ O) ₂]	<i>P2</i> ₁ / <i>n</i>	3D	✓	✗	Y. Gong <i>et al.</i> , <i>Inorg. Chem.</i> , 45 (2006) 4987-4995
15.	XOTRIJ	[Eu(HPam)]	<i>Pnma</i>	3D	✗	✓	R. Fu <i>et al.</i> , <i>Cryst. Growth Des.</i> , 14 (2014) 6197-6204

16.	XOTROP	[Tb(HPam)]	<i>Pnma</i>	3D	*	✓	R. Fu <i>et al.</i> , <i>Cryst. Growth Des.</i> , 14 (2014) 6197-6204
17.	XOTRUV	[Sm(HPam)]	<i>Pnma</i>	3D	*	✓	R. Fu <i>et al.</i> , <i>Cryst. Growth Des.</i> , 14 (2014) 6197-6204
18.	XOTSAC	[Nd(HPam)]	<i>P2₁/c</i>	3D	*	✓	R. Fu <i>et al.</i> , <i>Cryst. Growth Des.</i> , 14 (2014) 6197-6204
2. H₄Ale							
1.	EJEZUP	Li[(H ₃ Ale)(H ₂ O) ₂]	<i>P2₁/c</i>	org.-inorg. salt	*	✓	G. B. Deacon <i>et al.</i> , <i>J. Coord. Chem.</i> , 64 (2011) 179-185
2.	TEHWOS	Na(H ₃ Ale)·3H ₂ O	<i>P2₁/n</i>	org.-inorg. salt	✓	*	D. Vega <i>et al.</i> , <i>Acta Cryst.</i> , C52 (1996) 2198-2201
3.	PUQHAM	Na ₂ [(H ₂ Ale)(H ₂ O) ₄]·H ₂ O	<i>P2₁/c</i>	org.-inorg. salt	✓	*	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
4.	PUQFOY	2[K(H ₃ Ale)]·3H ₂ O	<i>P2₁/c</i>	org.-inorg. salt	✓	*	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
5.	PUQHEQ	K ₂ [(H ₂ Ale)(H ₂ O) ₆]	<i>P1</i>	org.-inorg. salt	✓	*	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
6.	PUQFUE	K ₂ [(H ₃ Ale) ₂ (H ₂ O) ₂]·2H ₂ O	<i>C2/c</i>	org.-inorg. salt	✓	*	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
7.	PUQGAL01	Rb[(H ₃ Ale)(H ₂ O)]·H ₂ O	<i>P2₁/c</i>	org.-inorg. salt	✓	*	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
8.	PUQGOZ	Rb[(H ₃ Ale)(H ₄ Ale)]·2H ₂ O	<i>P2₁/c</i>	org.-inorg. salt	✓	*	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
9.	PUQGAL	Rb ₂ [(H ₃ Ale) ₂ (H ₂ O) ₂]·2H ₂ O	<i>C2/c</i>	org.-inorg. salt	✓	*	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
10.	PUQHIU	Rb ₂ [(H ₂ Ale)(H ₂ O) ₅]·H ₂ O	<i>P2₁/n</i>	org.-inorg. salt	✓	*	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
11.	PUQHOA	Rb ₄ [(H ₂ Ale) ₂ (H ₂ O) ₈]·H ₂ O	<i>P1</i>	org.-inorg. salt	✓	*	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
12.	PUQGIT	Cs[(H ₃ Ale)(H ₂ O)]·H ₂ O	<i>P2₁/c</i>	org.-inorg. salt	✓	*	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662

13.	PUQGUF	Cs[(H ₃ Ale)(H ₄ Ale)]·2H ₂ O	$P\bar{1}$	org.-inorg. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
14.	PUQJAO	Cs ₂ [(H ₂ Ale)(H ₂ O) ₄]	$P\bar{1}$	org.-inorg. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
15.	PUQHUG	Cs ₄ [(H ₂ Ale) ₂ (H ₂ O) ₉]·2H ₂ O	$P\bar{1}$	org.-inorg. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>Cryst. Growth Des.</i> , 15 (2015) 4646-4662
16.	VEFBEQ	(H ₂ en)(H ₂ Ale)·2H ₂ O	<i>Pbca</i>	org.-org. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>CrystEngComm</i> , 19 (2017) 5611-5621
17.	VEFBIU	(H ₂ meen)(H ₂ Ale)·3H ₂ O	$P2_1/c$	org.-org. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>CrystEngComm</i> , 19 (2017) 5611-5621
18.	VEFBOA	(H ₂ me ₂ en)(H ₂ Ale)·3.5H ₂ O	$P2_1/n$	org.-org. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>CrystEngComm</i> , 19 (2017) 5611-5621
19.	VEFBUG	(H ₂ et ₂ en)(H ₂ Ale)·2H ₂ O	$P2_12_12_1$	org.-org. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>CrystEngComm</i> , 19 (2017) 5611-5621
20.	VEFCAN	(H ₂ chda)(H ₂ Ale)·3H ₂ O	$P\bar{1}$	org.-org. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>CrystEngComm</i> , 19 (2017) 5611-5621
21.	VEFCER	(H ₂ xda)(H ₂ Ale)·3H ₂ O	$P2_1/c$	org.-org. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>CrystEngComm</i> , 19 (2017) 5611-5621
22.	VEFCIV	(H ₂ oda)(H ₂ Ale)·2H ₂ O·0.5EtOH	$C2/c$	org.-org. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>CrystEngComm</i> , 19 (2017) 5611-5621
23.	VEFCOB	(Hphea) ₂ (H ₂ Ale)·2H ₂ O	$P\bar{1}$	org.-org. salt	✓	✗	G. B. Deacon <i>et al.</i> , <i>CrystEngComm</i> , 19 (2017) 5611-5621
24.	VEFCUH	(Hmel) ₂ (H ₂ Ale)·7H ₂ O	$P2_1/c$	org.-org. salt	✗	✓	G. B. Deacon <i>et al.</i> , <i>CrystEngComm</i> , 19 (2017) 5611-5621
25.	DILTEZ	[Cu(2,2'-bpy)(H ₃ Ale)(Cl)]·4H ₂ O	$C2/c$	0D	✓	✗	K. D. Demadis <i>et al.</i> , <i>Cryst. Growth Des.</i> , 13 (2013) 4480-4489
26.	ACUZUP	[Ni ₂ (H ₃ Ale) ₄ (H ₂ O) ₂]·2H ₂ O	$P2_1/c$	0D	✓	✓	M. Sikorska <i>et al.</i> , <i>Acta Cryst.</i> , E68 (2012) m820-m821
27.	FAZVOT	[Cu ₂ (H ₃ Ale) ₄ (H ₂ O) ₂]·2H ₂ O	$P2_1/c$	0D	✓	✓	B. Demoro <i>et al.</i> , <i>Dalton Trans.</i> , 41 (2012) 6468-6476
28.	ICUVOS	[Co ₂ (H ₃ Ale) ₄ (H ₂ O) ₂]·2H ₂ O	$P2_1/c$	0D	✓	✓	S. P. Man <i>et al.</i> , <i>Polyhedron</i> , 25 (2006) 1017-1032

29.	GIKPEW	[Mn(H ₂ Ale)]·H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	1D	✓	✗	Z.-C. Zhang <i>et al.</i> , <i>Inorg. Chem. Commun.</i> , 10 (2007) 1063-1066
30.	LILQII	[Ca(H ₂ Ale)]·H ₂ O	<i>P</i> 2 ₁ 2 ₁ 2 ₁	1D	✓	✗	E. Alvarez <i>et al.</i> , <i>CrystEngComm</i> , 15 (2013) 9899-9905
3. H₄Ner							
1.	ICUTOQ	[Co(H ₃ Ner) ₂ (H ₂ O) ₂]·2H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	0D	✓	✗	S. P. Man <i>et al.</i> , <i>Polyhedron</i> , 25 (2006) 1017-1032
2.	ICUTUW	[Ni(H ₃ Ner) ₂ (H ₂ O) ₂]·2H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	0D	✓	✗	S. P. Man <i>et al.</i> , <i>Polyhedron</i> , 25 (2006) 1017-1032
3.	ICUVAE	[Zn(H ₃ Ner) ₂ (H ₂ O) ₂]·2H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	0D	✓	✗	S. P. Man <i>et al.</i> , <i>Polyhedron</i> , 25 (2006) 1017-1032
4.	ICUVEI	[Mn ₂ (H ₃ Ner) ₄ (H ₂ O) ₂]·2H ₂ O	<i>P</i> 2 ₁ / <i>n</i>	0D	✓	✗	S. P. Man <i>et al.</i> , <i>Polyhedron</i> , 25 (2006) 1017-1032
5.	ICUVIM	[Cd ₂ (H ₃ Ner) ₄ (H ₂ O) ₂]·2H ₂ O	<i>P</i> 2 ₁ / <i>n</i>	0D	✓	✓	S. P. Man <i>et al.</i> , <i>Polyhedron</i> , 25 (2006) 1017-1032
4. H₄Zol							
1.	KUQYIF	Na ₃ [(H ₃ Zol) ₂ (H _{3.5} Zol) ₂ (H ₂ O) ₄]·2H ₂ O	<i>P</i> $\bar{1}$	org.-inorg. salt	✓	✗	E. Freire <i>et al.</i> , <i>Acta Cryst.</i> , C66 (2010) m122-m126
2.	DULFOG	K[(H ₃ Zol)(H ₂ O)]·H ₂ O	<i>P</i> $\bar{1}$	org.-inorg. salt	✓	✗	E. Freire <i>et al.</i> , <i>Acta Cryst.</i> , C66 (2010) m13-m16
3.	JAPJOC	(NH ₄) ₂ (H ₂ Zol)·2H ₂ O	<i>P</i> $\bar{1}$	org.-inorg. salt	✓	✗	M. Sikorska <i>et al.</i> , <i>J. Crystallogr.</i> , 2013 (2013) 1-5
4.	ENODIV	(Hcyt)(H ₃ Zol)·3H ₂ O	<i>P</i> $\bar{1}$	org.-org. salt	✓	✗	B. Sridhar <i>et al.</i> , <i>Acta Cryst.</i> , C67 (2011) o115-o119
5.	SIXZUW	(Hade) ₂ (H ₂ Zol)·4H ₂ O	<i>P</i> 2 ₁ / <i>n</i>	org.-org. salt	✓	✗	B. Sridhar <i>et al.</i> , <i>Acta Cryst.</i> , C70 (2014) 67-74
6.	SIYBAF	(Hade) ₂ (H ₂ Zol)·6H ₂ O	<i>P</i> $\bar{1}$	org.-org. salt	✓	✗	B. Sridhar <i>et al.</i> , <i>Acta Cryst.</i> , C70 (2014) 67-74
7.	YAGXEL	(Hdcha) ₃ (HZol)·H ₂ O·EtOH	<i>P</i> $\bar{1}$	org.-org. salt	✓	✗	A. Sarkar <i>et al.</i> , <i>Acta Cryst.</i> , E67 (2011) o2980
8.	TUVZAM	[Mg(H ₃ Zol) ₂ (H ₂ O) ₂]	<i>P</i> $\bar{1}$	0D	✓	✗	E. Freire <i>et al.</i> , <i>Acta Cryst.</i> , C66 (2010) m166-m170

9.	VIMXOF	[Co(H ₃ Zol) ₂ (H ₂ O) ₂]	$P\bar{1}$	0D	✓	✗	D.-K. Cao <i>et al.</i> , <i>Inorg. Chem.</i> , 46 (2007) 7571-7578
10.	VIMXUL	[Ni(H ₃ Zol) ₂ (H ₂ O) ₂]	$P\bar{1}$	0D	✓	✗	D.-K. Cao <i>et al.</i> , <i>Inorg. Chem.</i> , 46 (2007) 7571-7578
11.	RUPXAC	[Mn(H ₃ Zol) ₂ (H ₂ O) ₂]	$P\bar{1}$	0D	✓	✗	Z.-C. Zhang <i>et al.</i> , <i>Acta Cryst.</i> , E65 (2009) m1701-m1702
12.	PUFXUK	[Zn(H ₃ Zol) ₂ (H ₂ O) ₂]	$P\bar{1}$	0D	✓	✗	E. Freire <i>et al.</i> , <i>Acta Cryst.</i> , E65 (2009) m1428-m1429
13.	PUFYAR	[Zn(H ₃ Zol) ₂ (H ₂ O)]·2H ₂ O	$C2/c$	0D	✓	✗	E. Freire <i>et al.</i> , <i>Acta Cryst.</i> , E65 (2009) m1430-m1431
14.	DOGYII	[Cu(H ₃ Zol) ₂]	$P\bar{1}$	0D	✓	✗	D.-K. Cao <i>et al.</i> , <i>Dalton Trans.</i> , 0 (2008) 5008-5015
15.	DOGYEE	[Cu(H ₃ Zol) ₂ (H ₂ O)]·2H ₂ O	$C2/c$	0D	✓	✗	D.-K. Cao <i>et al.</i> , <i>Dalton Trans.</i> , 0 (2008) 5008-5015
16.	IMUTUH	[Cu(2,2'-bpy)(H ₃ Zol)(HSO ₄)]	$P\bar{1}$	0D	✓	✗	Q.-J. Niu <i>et al.</i> , <i>J. Coord. Chem.</i> , 69 (2016) 1447-1462
17.	IMUVAP	[Cu ₂ (2,2'-bpy) ₂ (HZol)(H ₂ O)(Cl)]·4H ₂ O	$P\bar{1}$	0D	✓	✗	Q.-J. Niu <i>et al.</i> , <i>J. Coord. Chem.</i> , 69 (2016) 1447-1462
18.	IMUVET	[Cu ₂ (phen) ₂ (HZol)(H ₂ O)(Cl)]·2.5H ₂ O	$C2/c$	0D	✓	✗	Q.-J. Niu <i>et al.</i> , <i>J. Coord. Chem.</i> , 69 (2016) 1447-1462
19.	IMUVIX	[Cu ₃ (2,2'-bpy) ₃ (H ₃ Zol)(HZol)(SO ₄)]·5H ₂ O	$P\bar{1}$	0D	✓	✗	Q.-J. Niu <i>et al.</i> , <i>J. Coord. Chem.</i> , 69 (2016) 1447-1462
20.	POXCOW	Na ₂ [Re(CO) ₃ (2,2'-bpy)(H ₃ Zol)]Cl ₃ ·8H ₂ O	$P\bar{1}$	0D	✓	✗	A. Yazdani <i>et al.</i> , <i>Inorg. Chem.</i> , 54 (2015) 1728-1736
21.	FELZAZ	Fe ₁₅ (HZol) ₁₀ (H ₂ Zol) ₂ (H ₂ O) ₂₄ (2/3Cl:1/3H ₂ O) ₆ ·7Cl·65(H ₂ O)	$P\bar{1}$	0D	✓	✗	E. Freire <i>et al.</i> , <i>Inorganica Chim. Acta</i> , 394 (2013) 229-236
22.	TAMMEB	[Ca(H ₂ Zol)(H ₂ O)]	$Pna2_1$	1D	✓	✗	D. Liu <i>et al.</i> , <i>Chem. Commun.</i> , 48 (2012) 2668-2670
23.	GOZPUI	[Cu ₃ (HZol) ₂ (H ₂ O) ₆]·6H ₂ O	$P\bar{1}$	1D	✓	✗	L. Qiu <i>et al.</i> , <i>Eur. J. Med. Chem.</i> , 89 (2015) 42-50
24.	OXAMUW	[Mn(H ₂ Zol)]·H ₂ O	$P2_1/c$	1D	✓	✗	D.-K. Cao <i>et al.</i> , <i>Inorg. Chem.</i> , 50 (2011) 2278-2287

25.	VIRXAX	(H ₂ ppz)[Zn ₂ (HZol) ₂ (ox)]	$P\bar{1}$	1D	✓	✗	X.-L. Zhang <i>et al.</i> , <i>Dalton Trans.</i> , 43 (2014) 285-289
26.	VIMXIZ	[Ni ₃ (HZol) ₂ (H ₂ O) ₄] \cdot 2H ₂ O	$P\bar{1}$	2D	✓	✗	D.-K. Cao <i>et al.</i> , <i>Inorg. Chem.</i> , 46 (2007) 7571-7578
27.	VIMXEV	[Co ₃ (HZol) ₂ (H ₂ O) ₄] \cdot 2H ₂ O	$P\bar{1}$	2D	✓	✗	D.-K. Cao <i>et al.</i> , <i>Inorg. Chem.</i> , 46 (2007) 7571-7578
28.	VIRXEB	[Zn ₃ (HZol) ₂ (H ₂ O) ₄]	$C2/c$	2D	✓	✗	X.-L. Zhang <i>et al.</i> , <i>Dalton Trans.</i> , 43 (2014) 285-289
29.	OXAMOQ	[Co ₃ (HZol) ₂ (H ₂ O) ₄]	$C2/c$	2D	✓	✗	D.-K. Cao <i>et al.</i> , <i>Inorg. Chem.</i> , 50 (2011) 2278-2287
30.	DOGYUU01	[Cu ₃ (HZol) ₂ (H ₂ O) ₂]	$P\bar{1}$	2D	✓	✗	Y. Li, <i>Acta Cryst.</i> , E66 (2010) m1576
31.	KUJGON	(H ₂ en)[Co ₃ (H ₂ Zol) ₂ (ox)(H ₂ O) ₂]	$P\bar{1}$	2D	✓	✗	Q.-J. Niu <i>et al.</i> , <i>J. Solid State Chem.</i> , 227 (2015) 212-218
32.	OXAMIK	[Co ₃ (HZol) ₂ (H ₂ O) ₄] \cdot 2H ₂ O	$P\bar{1}$	3D	✓	✗	D.-K. Cao <i>et al.</i> , <i>Inorg. Chem.</i> , 50 (2011) 2278-2287
33.	AKUKUO	[Ni ₃ (HZol) ₂ (bpe) ₂] \cdot 4H ₂ O	$P\bar{1}$	3D	✓	✗	Q.-J. Niu <i>et al.</i> , <i>Transit. Met. Chem.</i> , 41 (2016) 365-373
34.	SUSMIE	[Ni ₃ (HZol) ₂ (4,4'-bpy)] \cdot (4,4'-bpy) \cdot 4H ₂ O	$P\bar{1}$	3D	✓	✗	X.-Q. Wu <i>et al.</i> , <i>Inorg. Chem. Commun.</i> , 58 (2015) 60-63
35.	VIRXIF	(H ₂ ppz)[Zn ₃ (Zol) ₂]	$P3_221$	3D	✓	✗	X.-L. Zhang <i>et al.</i> , <i>Dalton Trans.</i> , 43 (2014) 285-289
36.	KUJGUT	[Cd ₄ (HZol) ₂ (ox)(H ₂ O) ₂]	$C2/c$	3D	✓	✗	Q.-J. Niu <i>et al.</i> , <i>J. Solid State Chem.</i> , 227 (2015) 212-218
5. H₄Ris							
1.	WURPOO	Na(H ₃ Ris) \cdot 2H ₂ O	$P\bar{1}$	org.-inorg. salt	✓	✗	W. L. Gossman <i>et al.</i> , <i>Acta Cryst.</i> , C59 (2003) m33-m36
2.	WURPUU	Na(H ₃ Ris) \cdot 2.5H ₂ O	$C2/c$	org.-inorg. salt	✓	✗	W. L. Gossman <i>et al.</i> , <i>Acta Cryst.</i> , C59 (2003) m33-m36
3.	ORUWII	3[Na(H ₃ Ris)] \cdot 3AcOH	$P2_1/n$	org.-inorg. salt	✓	✗	J. Bruning <i>et al.</i> , <i>J. Pharm. Sci.</i> , 100 (2011) 863-873

4.	YEFTOT	$\text{K}(\text{H}_3\text{Ris})\cdot 2\text{H}_2\text{O}$	$P2_1/n$	org.-inorg. salt	✓	✗	K. Stahl <i>et al.</i> , <i>Acta Cryst.</i> , C62 (2006) m112-m115
5.	YEFTIN	$(\text{NH}_4)(\text{H}_3\text{Ris})\cdot 2\text{H}_2\text{O}$	$P2_1/n$	org.-inorg. salt	✓	✗	K. Stahl <i>et al.</i> , <i>Acta Cryst.</i> , C62 (2006) m112-m115
6.	LUVMUL	$[\text{Cu}(\text{H}_3\text{Ris})_2]\cdot 4\text{H}_2\text{O}$	$P\bar{1}$	0D	✓	✗	S. Kunnas-Hiltunen <i>et al.</i> , <i>Z. Anorg. Allg. Chem.</i> , 636 (2010) 710-720
7.	LAKPOE	$[\text{Ni}(\text{H}_3\text{Ris})_2(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$	$P\bar{1}$	0D	✓	✗	B. Demoro <i>et al.</i> , <i>J. Inorg. Biochem.</i> , 104 (2010) 1252-1258
8.	DUPXOC	$[\text{Zn}(\text{H}_2\text{Ris})]$	$P2_1/n$	1D	✓	✗	X. Huang <i>et al.</i> , <i>Acta Cryst.</i> , E66 (2010) m59-m60
9.	POLNEK	$[\text{Cd}(\text{H}_2\text{Ris})(\text{H}_2\text{O})]$	$P2_12_12_1$	1D	✓	✗	J. Hu <i>et al.</i> , <i>Inorg. Chem. Commun.</i> , 11 (2008) 1110-1112
10.	GAPSIC	$[\text{Cd}(\text{H}_2\text{Ris})]\cdot \text{H}_2\text{O}$	$P2_1/c$	1D	✓	✗	K.-R. Ma <i>et al.</i> , <i>J. Mol. Struct.</i> , 1139 (2017) 67-77
11.	HIRJUP	$[\text{Fe}(\text{H}_2\text{Ris})(\text{H}_2\text{O})]$	$P2_1/n$	1D	✓	✗	K.-R. Ma <i>et al.</i> , <i>Synth. Met.</i> , 182 (2013) 40-48
12.	MINKEA	$[\text{Co}(\text{H}_2\text{Ris})(\text{H}_2\text{O})]$	$P2_1/n$	1D	✓	✗	Z.-C. Zhang <i>et al.</i> , <i>Dalton Trans.</i> , 0 (2007) 4681-4684
13.	PUNZII	$[\text{Mn}(\text{H}_2\text{Ris})(\text{H}_2\text{O})]$	$P2_1/n$	1D	✓	✗	J. Zhao <i>et al.</i> , <i>Inorg. Chim. Acta</i> , 363 (2010) 662-668
14.	YUDPAP	$[\text{Mn}(\text{H}_2\text{Ris})]\cdot 3\text{H}_2\text{O}$	$P\bar{1}$	1D	✓	✗	Y. Ma <i>et al.</i> , <i>Inorg. Chem. Commun.</i> , 12 (2009) 860-863
15.	GAPSUO	$[\text{Cu}_3(\text{H}_3\text{Ris})_4]\cdot 2(\text{OH})\cdot 2\text{H}_2\text{O}$	$P\bar{1}$	1D	✓	✗	K.-R. Ma <i>et al.</i> , <i>J. Mol. Struct.</i> , 1139 (2017) 67-77
16.	RUFFAB	$(\text{Hdma})[\text{Zn}_2(\text{H}_2\text{Ris})(\text{HRis})]\cdot 3\text{H}_2\text{O}$	$P2_1/c$	1D	✓	✗	T. Sun <i>et al.</i> , <i>RSC Adv.</i> , 5 (2015) 26410-26419
17.	HIRJOJ	$[\text{Mg}_3(\text{HRis})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$	$P\bar{1}$	2D	✓	✗	K.-R. Ma <i>et al.</i> , <i>Synth. Met.</i> , 182 (2013) 40-48
18.	GAPSOI	$[\text{Cu}_3(\text{HRis})_2(\text{H}_2\text{O})_2]$	$P2_1/c$	2D	✓	✗	K.-R. Ma <i>et al.</i> , <i>J. Mol. Struct.</i> , 1139 (2017) 67-77
19.	HIYBAU	$[\text{Ni}_3(\text{HRis})_2(\text{H}_2\text{O})_4]\cdot \text{H}_2\text{O}$	$P\bar{1}$	2D	✗	✓	Z.-F. Guo <i>et al.</i> , <i>Transit. Met. Chem.</i> , 39 (2014) 353-360

20.	PUNZEE	[Ni ₃ (HRis) ₂ (H ₂ O) ₄] \cdot 2H ₂ O	$P\bar{1}$	2D	✓	✗	J. Zhao <i>et al.</i> , <i>Inorg. Chim. Acta</i> , 363 (2010) 662-668
21.	HIRKAW	[Ni ₃ (HRis) ₂ (H ₂ O) ₄] \cdot 3H ₂ O	$P\bar{1}$	2D	✗	✓	K.-R. Ma <i>et al.</i> , <i>Synth. Met.</i> , 182 (2013) 40-48
22.	POLNIO	[Cd ₂ (HRis)(H ₂ O)(Cl)]	$P2_1/c$	2D	✓	✗	J. Hu <i>et al.</i> , <i>Inorg. Chem. Commun.</i> , 11 (2008) 1110-1112
23.	HIXZUL	[Cu ^I Cu ^{II} (HRis)] \cdot (H ₂ O) \cdot 0.5(en)	$P\bar{1}$	2D	✓	✗	Z.-F. Guo <i>et al.</i> , <i>Transit. Met. Chem.</i> , 39 (2014) 353-360
24.	VEGWOV	[Fe ₃ (H ₂ Ris) ₂ (H ₂ O) ₂ (ox)]	$P\bar{1}$	2D	✓	✗	C. Li <i>et al.</i> , <i>CrystEngComm</i> , 14 (2012) 5479-5486
25.	VEGWUB	[Co ₃ (H ₂ Ris) ₂ (H ₂ O) ₂ (ox)]	$P\bar{1}$	2D	✓	✗	C. Li <i>et al.</i> , <i>CrystEngComm</i> , 14 (2012) 5479-5486
26.	VEGXAI	[Zn ₃ (H ₂ Ris) ₂ (H ₂ O) ₂ (ox)]	$P\bar{1}$	2D	✓	✗	C. Li <i>et al.</i> , <i>CrystEngComm</i> , 14 (2012) 5479-5486
27.	VEGXEM	[Cu ₃ (H ₂ Ris) ₂ (ox)]	$P\bar{1}$	2D	✓	✗	C. Li <i>et al.</i> , <i>CrystEngComm</i> , 14 (2012) 5479-5486
28.	TAPJUR	[Zn ₂ (Ris)(H ₂ O)]	$P2_1/n$	3D	✓	✗	R. Fu <i>et al.</i> , <i>CrystEngComm</i> , 13 (2011) 2331-2335
29.	TAPKAY	[Cu ₄ (Ris) ₂ (H ₂ O) ₄] \cdot 1.25H ₂ O	$P\bar{1}$	3D	✓	✗	R. Fu <i>et al.</i> , <i>CrystEngComm</i> , 13 (2011) 2331-2335
30.	TIGSOT	(H ₂ dmtppz) _{0.5} [Zn ₃ (Ris)(HRis)] \cdot 3H ₂ O	$P2_1/c$	3D	✓	✗	R. Fu <i>et al.</i> , <i>CrystEngComm</i> , 13 (2011) 6334-6336
31.	RUFDUT	(Hdma) ₂ [Ni ₃ (Ris) ₂ (H ₂ O) ₂] \cdot 2H ₂ O	$Pbca$	3D	✓	✗	T. Sun <i>et al.</i> , <i>RSC Adv.</i> , 5 (2015) 26410-26419
32.	LICKAL	(H ₂ ampy) _{0.5} [Zn ₃ (Ris)(HRis)] \cdot 3H ₂ O	$P2_1/c$	3D	✓	✗	R. Fu <i>et al.</i> , <i>CrystEngComm</i> , 13 (2011) 6334-6336
6. H₄Py-Ris							
1.	OGATIB	[Cu(H ₃ 4py-Ris) ₂]	$P2_1/c$	0D	✓	✗	Y.-S. Ma <i>et al.</i> , <i>RSC Adv.</i> , 3 (2013) 18430-18440
2.	ODEPAR	[Zn(H ₂ 4py-Ris)] \cdot H ₂ O	$P2_1/c$	1D	✓	✗	W.-Y. Yin <i>et al.</i> , <i>J. Mol. Eng. Mater.</i> , 2 (2014) 1440003

3.	ODEPEV	[Cd(H ₂ 4py-Ris)]·H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	1D	✓	✗	W.-Y. Yin <i>et al.</i> , <i>J. Mol. Eng. Mater.</i> , 2 (2014) 1440003
4.	OGASOG	[Mn(H ₂ 4py-Ris)]·H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	1D	✓	✗	Y.-S. Ma <i>et al.</i> , <i>RSC Adv.</i> , 3 (2013) 18430-18440
5.	OGATUN	[Co(H ₂ 4py-Ris)]·H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	1D	✓	✗	Y.-S. Ma <i>et al.</i> , <i>RSC Adv.</i> , 3 (2013) 18430-18440
6.	OGATAT	[Cu(H ₂ 4py-Ris)]	<i>P</i> 1̄	1D	✓	✗	Y.-S. Ma <i>et al.</i> , <i>RSC Adv.</i> , 3 (2013) 18430-18440
7.	OGATOH	[Co ₂ (H ₃ 4py-Ris) ₂ (ox)(H ₂ O) ₂]·2H ₂ O	<i>P</i> 1̄	1D	✓	✗	Y.-S. Ma <i>et al.</i> , <i>RSC Adv.</i> , 3 (2013) 18430-18440
8.	OGASUM	[Cu ^I Cu ^{II} ₃ (H _{0.5} 4-pyRis) ₂]	<i>P</i> 1̄	2D	✓	✗	Y.-S. Ma <i>et al.</i> , <i>RSC Adv.</i> , 3 (2013) 18430-18440
9.	OGATEX	[Cu ₃ (H ₂ 4py-Ris) ₂ (ox)]	<i>P</i> 1̄	2D	✓	✗	Y.-S. Ma <i>et al.</i> , <i>RSC Adv.</i> , 3 (2013) 18430-18440
10.	OGAVAV	[Co ₃ (H ₄ py-Ris) ₂ (ox)(H ₂ O) ₂]	<i>P</i> 1̄	2D	✓	✗	Y.-S. Ma <i>et al.</i> , <i>RSC Adv.</i> , 3 (2013) 18430-18440
7. H₄Min							
1.	ESAVAX ^d	[Zn(H ₃ Min) ₂ (H ₂ O) ₂]·3H ₂ O	<i>C</i> 2/ <i>c</i>	0D	✗	✗	R. Fu <i>et al.</i> , <i>Cryst. Growth Des.</i> , 16 (2016) 5074–5083
2.	ESAVEB	[Zn(H ₂ Min)(H ₂ O) ₂]·H ₂ O	<i>P</i> 2 ₁ / <i>c</i>	0D	✓	✗	R. Fu <i>et al.</i> , <i>Cryst. Growth Des.</i> , 16 (2016) 5074–5083
3.	ESATUP	[Zn(H ₂ Min)]	<i>Pca</i> 2 ₁	2D	✓	✗	R. Fu <i>et al.</i> , <i>Cryst. Growth Des.</i> , 16 (2016) 5074–5083
8. H₄Tra							
1.	POVRIC	[Co(H ₂ Tra)]	<i>P</i> 1̄	2D	✓	✗	D.-G. Ding <i>et al.</i> , <i>Cryst. Growth Des.</i> , 9 (2009) 508-516
2.	POVROI ^e	[Ni ₂ (H ₂ Tra) ₂](en)	<i>P</i> 2 ₁ / <i>c</i>	2D	✗	✗	D.-G. Ding <i>et al.</i> , <i>Cryst. Growth Des.</i> , 9 (2009) 508-516
3.	POVRAU	[Mn ₂ (Tra)(H ₂ O) ₂]	<i>P</i> 2 ₁ / <i>c</i>	3D	✓	✗	D.-G. Ding <i>et al.</i> , <i>Cryst. Growth Des.</i> , 9 (2009) 508-516
4.	POVREY	[Cu ₂ (Tra)(H ₂ O)]	<i>P</i> 1̄	3D	✓	✗	D.-G. Ding <i>et al.</i> , <i>Cryst. Growth Des.</i> , 9 (2009) 508-516

9. H₄Olp

no crystal structure based on H₄Olp was found in CSD

10. H₄Prp

no crystal structure based on H₄Prp was found in CSD

11. H₄Ppp

no crystal structure based on H₄Ppp was found in CSD

^aAbbreviations: H₄Pam – pamidronic acid, H₄Ale – alendronic acid, H₄Ner – neridronic acid, H₄Zol – zoledronic acid, H₄Ris – risedronic acid, H₄4Py-Ris – 1-hydroxy-2-(4-pyridyl)ethylidene-1,1-diphosphonic acid, H₄Min – minodronic acid, H₄Tra – 1-hydroxy-2-(1*H*-1,2,4-triazol-1-yl)ethylidene-1,1-diphosphonic acid, H₄Olp – olpadronic acid, H₄Prp – 1-hydroxy-3-(1-pyrrolidinyl)propylidene-1,1-diphosphonic acid, H₄Ppp – 1-hydroxy-3-(1-piperidinyl)propylidene-1,1-diphosphonic acid, ade – adenine, cyt – cytosine, gua – guanidine, 2,2'-bpy – 2,2'-bipyridine, 4,4'-bpy – 4,4'-bipyridine, bpe – trans-4,4'-vinylenedipyridine, phen – 1,10-phenanthroline, ampy – 4-(aminomethyl)pyridine, ppz – piperazine, dmtppz – 2,5-dimethylpiperazine, dma – dimethylamine, dcha – dicyclohexylamine, tba – tetrabutylammonium, en – ethylenediamine, meen – *N*-methylethylenediamine, me₂en – *N,N'*-dimethylethylenediamine, et₂en – *N,N'*-diethylethylenediamine, oda – 1,8-octanediamine, chda – cyclohexyl-1,2-diamine, xda – 1,3-benzenedimethanamine, phea – phenethylamine, mel – melamine, AcOH – acetic acid, H₂ox – oxalic acid, EtOH – ethanol. ^bConformation state was determined for the $\tau_1(\text{R}-\text{C}_\alpha-\text{C}-\text{O})$ dihedral angle describing the position of hydroxyl O atom with respect to the R¹ group: I – synclinal (*sc*), II – antiperiplanar (*ap*). ^cOne of crystallographically nonequivalent ligands in synperiplanar (*sp*) conformation. ^dLigand moiety in synperiplanar (*sp*) conformation. ^eLigand moiety in anticlinal (*ac*) conformation.

Table S2. Values of $\tau_1(\text{R}-\text{C}_\alpha-\text{C}-\text{O})$ dihedral angle in bisphosphonate ligands.

<i>Lp.</i>	<i>Database refcode</i>	$\pm\tau_1$ [°]	<i>Lp.</i>	<i>Database refcode</i>	$\pm\tau_1$ [°]	<i>Lp.</i>	<i>Database refcode</i>	$\pm\tau_1$ [°]	<i>Lp.</i>	<i>Database refcode</i>	$\pm\tau_1$ [°]
Ligands			11.	XEHTEK	52.57	13.	PUQGUF	63.75	3.	ICUVAE cd	50.50
1.	SOPSEV	66.54	12.	BACMUP	6.64	14.	PUQJAO	64.40	4.	ICUVEI	64.20
	GOWZEX	54.96			69.22			66.05			46.14
2.	KOJGUL	69.86	13.	XEHTUA	179.17	15.	PUQHUG	66.35	5.	ICUVIM	65.58
		65.99	14.	XEHTIO	67.19			59.91			168.22
3.	VUYTUE	52.26	15.	XOTRIJ	180.00	16.	VEFBEQ	53.54	4. H₄Zol		
4.	MEYGII	72.57	16.	XOTROP	180.00	17.	VEFBIU	65.30	1.	KUQYIF	51.34
	BEKBOJ	58.70	17.	XOTRUV	180.00	18.	VEFBOA	64.45			75.53
		51.69	18.	XOTSAC	178.90	19.	VEFBUG	60.01	2.	DULFOG	55.28
	ORUZEH	61.58	2. H₄Ale			20.	VEFCAN	61.09	3.	JAPJOC	60.37
5.	MOFVOS	59.31	1.	EJEZUP	177.89		62.19		4.	ENODIV	62.86
6.	UPAVUD	61.71	2.	TEHWOS	59.34	21.	VEFCER	69.89	5.	SIXZUW	53.93
7.	BIZWAI02	50.26	3.	PUQHAM	67.87	22.	VEFCIV	52.20	6.	SIYBAF	51.96
8.	WETQES	65.54	4.	PUQFOY	64.38	23.	VEFCOB	51.97	7.	YAGXEL	57.83
9.	FURCAW	179.01			69.30			51.49	63.13		
10.	GADPAD	162.10	5.	PUQHEQ	63.94	24.	VEFCUH	178.99	9.	VIMXOF	63.17
11.	EMIGIQ	70.29			64.09	25.	DILTEZ	35.48	10.	VIMXUL	62.53
1. H₄Pam			6.	PUQFUE	60.35	26.	ACQZUP	161.48	11.	RUPXAC	64.50
1.	FENREW	63.66		69.99	49.42	27.	FAZVOT	163.58	12.	PUFXUK	62.22
2.	EFAMIH	59.67	7.	PUQGAL01	62.12			49.19	39.83		
3.	IDAWIV	31.89	8.	PUQGOZ	68.76	28.	ICUVOS	161.82	13.	PUFYAR	39.83
4.	INIYUZ	32.32			67.57			50.87	14.	DOGYII	63.30
5.	FAZVUZ	31.70	9.	PUQGAL	60.23	29.	GIKPEW	57.82	15.	DOGYEE	41.32
6.	XEHTOU	35.67			69.70			30.	LILQII	45.92	16.
		169.77	10.	PUQHUI	67.41	17.	IMUVAP			57.35	
7.	DILTID	67.05	11.	PUQHOA	68.98	3. H₄Ner			18.	IMUVET	52.76
8.	KEVVOX01	59.64			56.32	1.	ICUTOQ	58.50	19.	IMUVIX	64.80
9.	TAMMAX	54.13	12.	PUQGIT	63.81	2.	ICUTUW	56.28	20.	POXCOW	60.19
10.	XEHTAG	51.31				3.	ICUVAE	31.58			

<i>Lp.</i>	<i>Database refcode</i>	$\pm\tau_1$ [°]	<i>Lp.</i>	<i>Database refcode</i>	$\pm\tau_1$ [°]	<i>Lp.</i>	<i>Database refcode</i>	$\pm\tau_1$ [°]
21.	FELZAZ	59.82	7.	LAKPOE	56.78	32.	LICKAL cd	66.95
		58.79	8.	DUPXOC	53.23	6. H₄Py-Ris		
		57.01	9.	POLNEK	58.97	1.	OGATIB	64.26
		62.78	10.	GAPSIC	69.19	2.	ODEPAR	59.06
		55.03	11.	HIRJUP	41.05	3.	ODEPEV	59.94
		59.42	12.	MINKEA	42.52	4.	OGASOG	60.52
22.	TAMMEB	52.95	13.	PUNZII	40.68	5.	OGATUN	61.29
23.	GOZPUI	61.10	14.	YUDPAP	62.06	6.	OGATAT	88.47
24.	OXAMUW	50.45	15.	GAPSUO	59.92	7.	OGATOH	46.60
25.	VIRXAX	58.83			49.39	8.	OGASUM	40.12
26.	VIMXIZ	55.45	16.	RUFFAB	66.70	9.	OGATEX	72.09
27.	VIMXEV	55.12			60.51	10.	OGAVAV	73.19
28.	VIRXEB	42.30	17.	HIRJOJ	62.96	7. H₄Min		
29.	OXAMOQ	41.81	18.	GAPSOI	56.03	1.	ESAVAX	24.37
30.	DOGYUU01	56.47	19.	HIYBAU	176.17	2.	ESAVEB	33.90
31.	KUJGON	35.13	20.	PUNZEE	62.86	3.	ESATUP	44.15
32.	OXAMIK	57.12	21.	HIRKAW	176.94	8. H₄Tra		
33.	AKUKUO	64.95	22.	POLNIO	64.53	1.	POVRIC	66.54
34.	SUSMIE	64.14	23.	HIXZUL	57.31	2.	POVROI	91.99
35.	VIRXIF	63.31	24.	VEGWOV	66.41	3.	POVRAU	38.78
36.	KUJGUT	71.08	25.	VEGWUB	68.09	4.	POVREY	41.06
5. H₄Ris			26.	VEGXAI	67.96	9. H₄Olp		
1.	WURPOO	53.94	27.	VEGXEM	68.45	–		
2.	WURPUU	67.22	28.	TAPJUR	46.88	10. H₄Prp		
3.	ORUWII	55.76	29.	TAPKAY	72.41	–		
		64.73			11. H₄PPP			
		63.00	72.75	–				
4.	YEFTOT	66.88	30.	TIGSOT	69.11			
5.	YEFTIN	58.11	31.	RUFDUT	40.91			
6.	LUVMUL	33.09	32.	LICKAL	75.22			

X-ray powder pattern for 1a

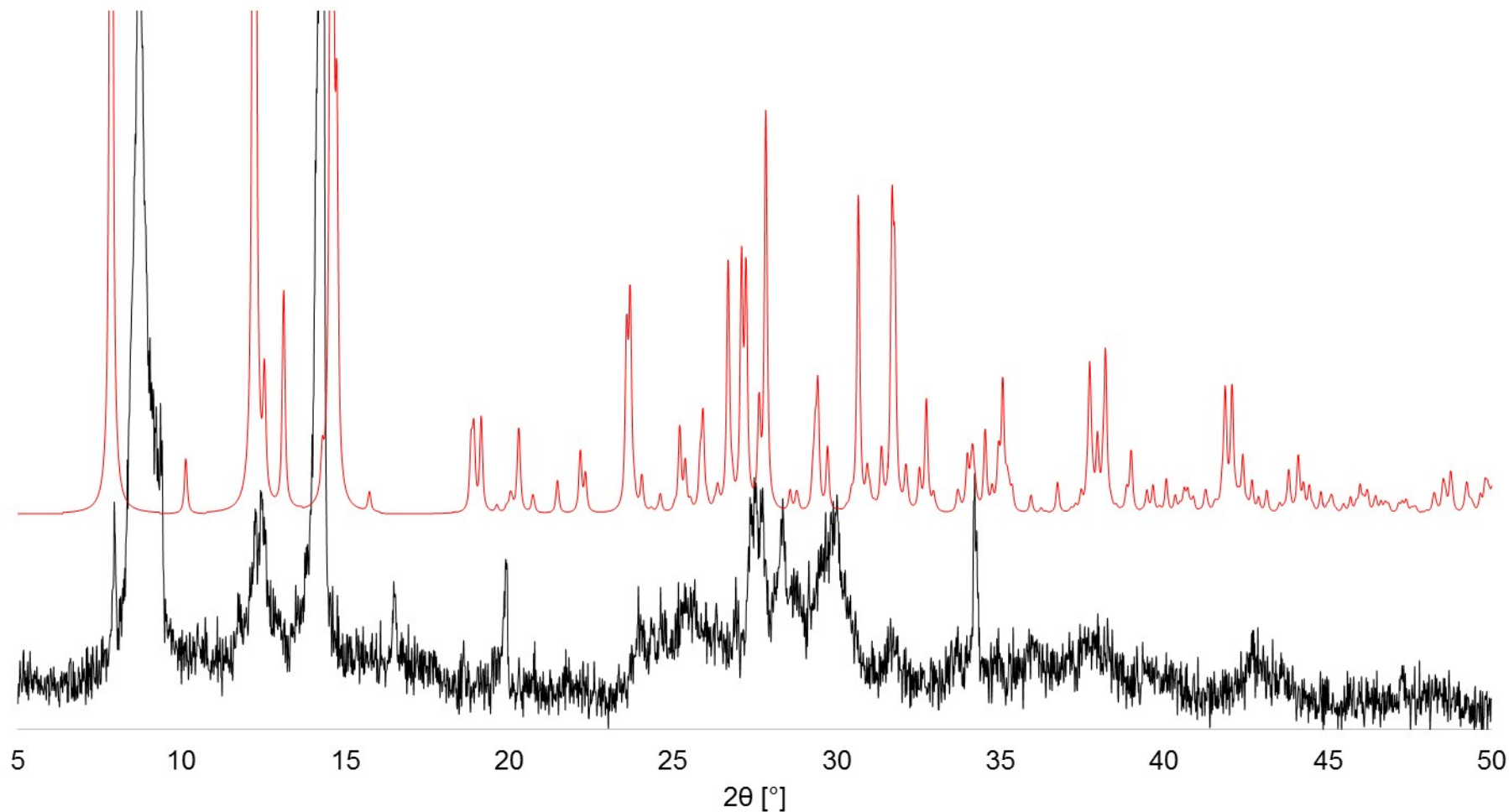


Figure S1. Experimental X-ray powder pattern (black, $T = 298$ K, $\text{Cu-K}\alpha$) and simulated powder pattern (red, $T = 100$ K, $\text{Mo-K}\alpha$) based on the results from single-crystal X-ray diffraction for the coordination unit **1a**.

X-ray powder pattern for 3a

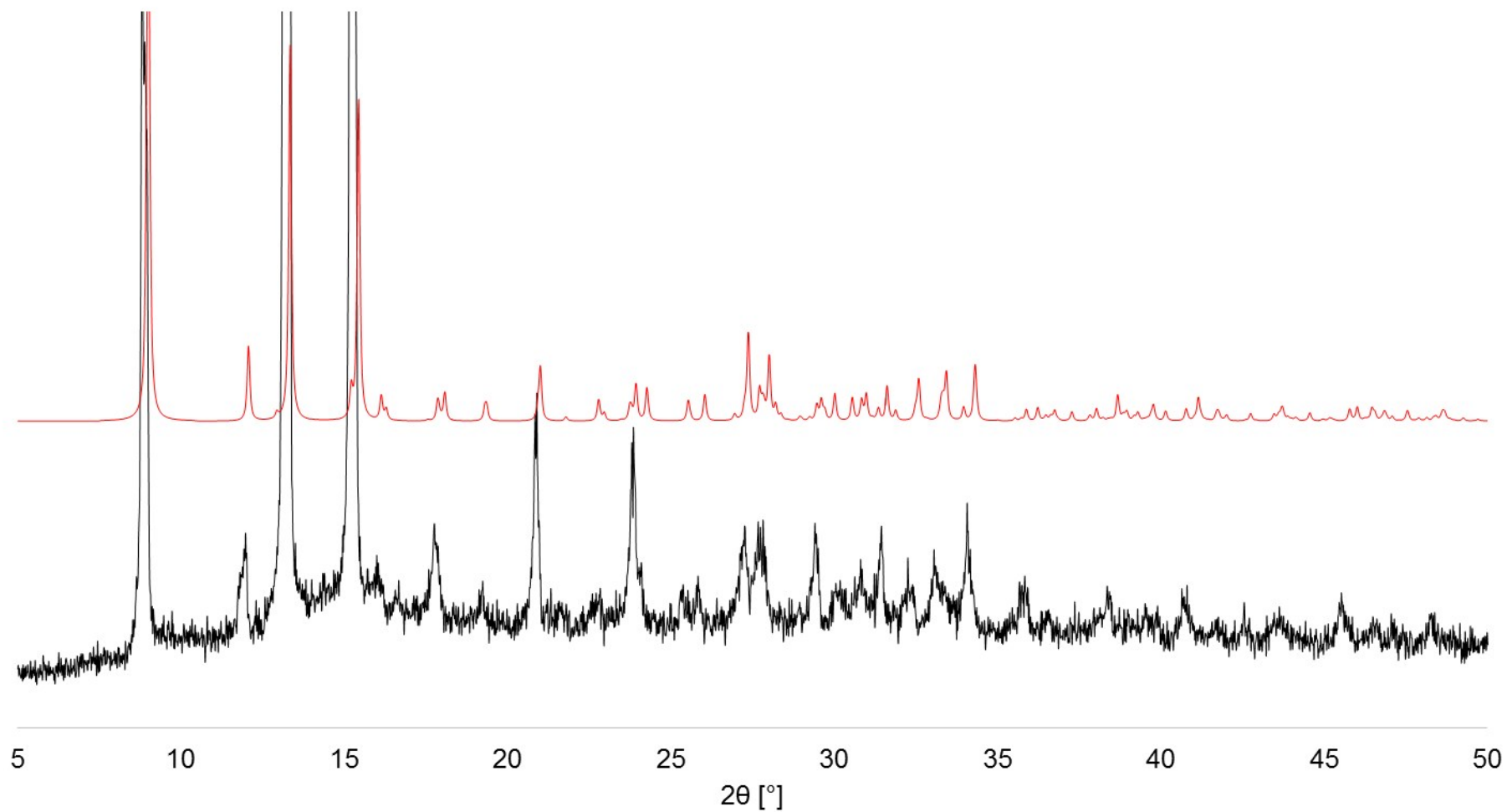


Figure S2. Experimental X-ray powder pattern (black, $T = 298$ K, $\text{Cu-K}\alpha$) and simulated powder pattern (red, $T = 100$ K, $\text{Mo-K}\alpha$) based on the results from single-crystal X-ray diffraction for the coordination unit **3a**.

X-ray powder pattern for 4a

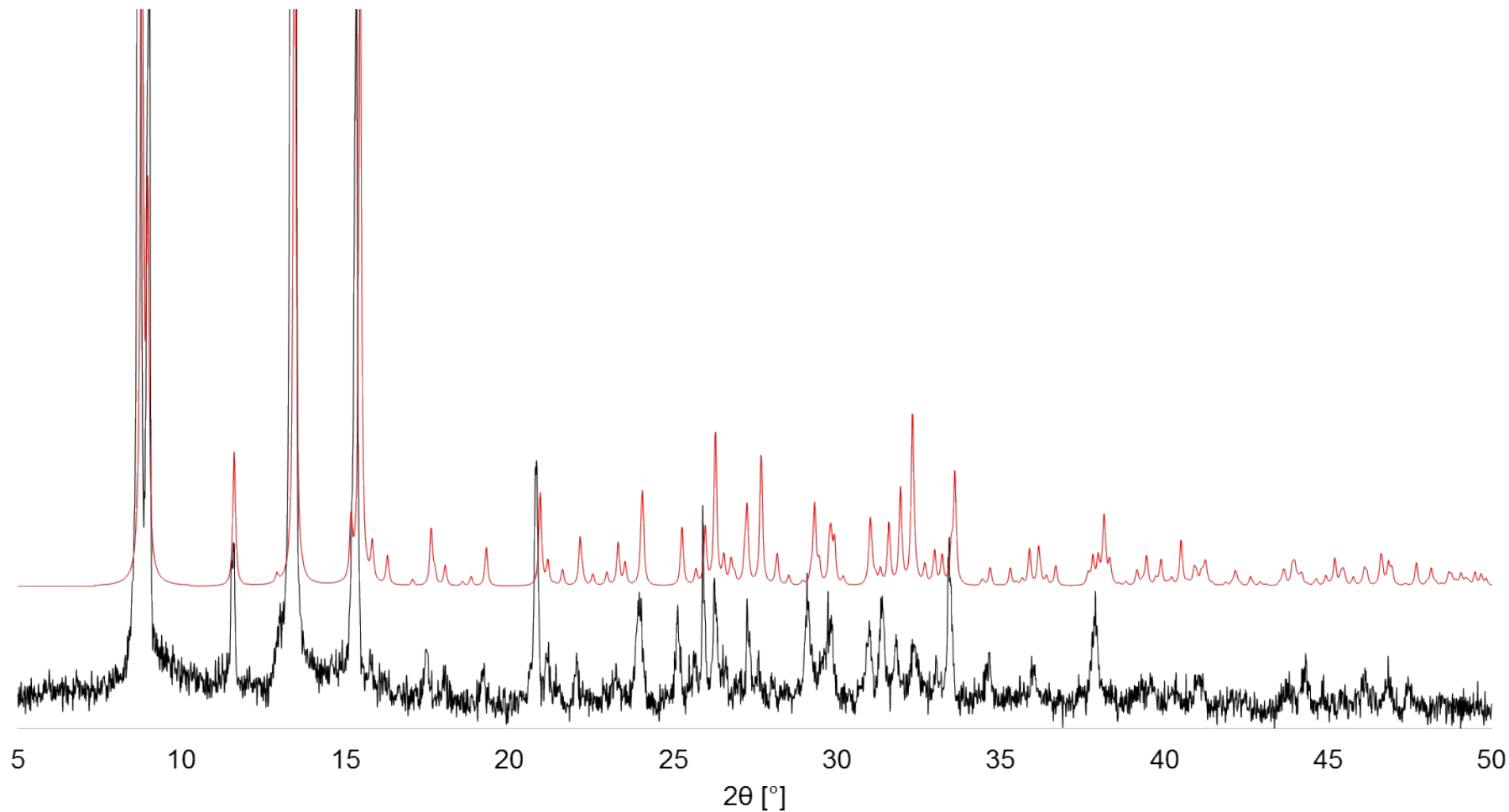
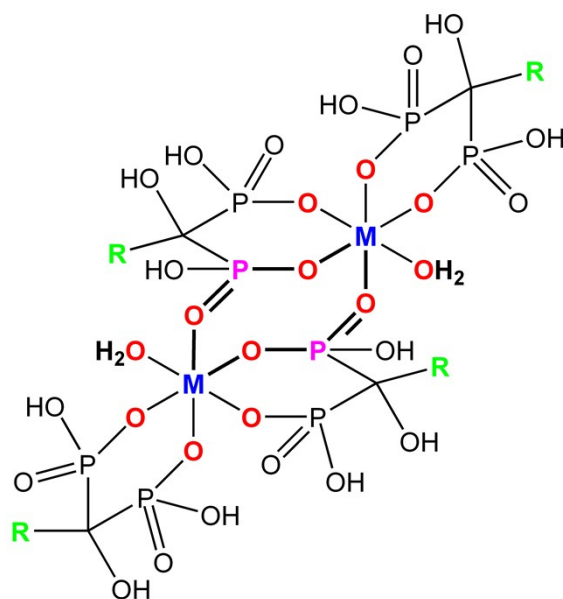
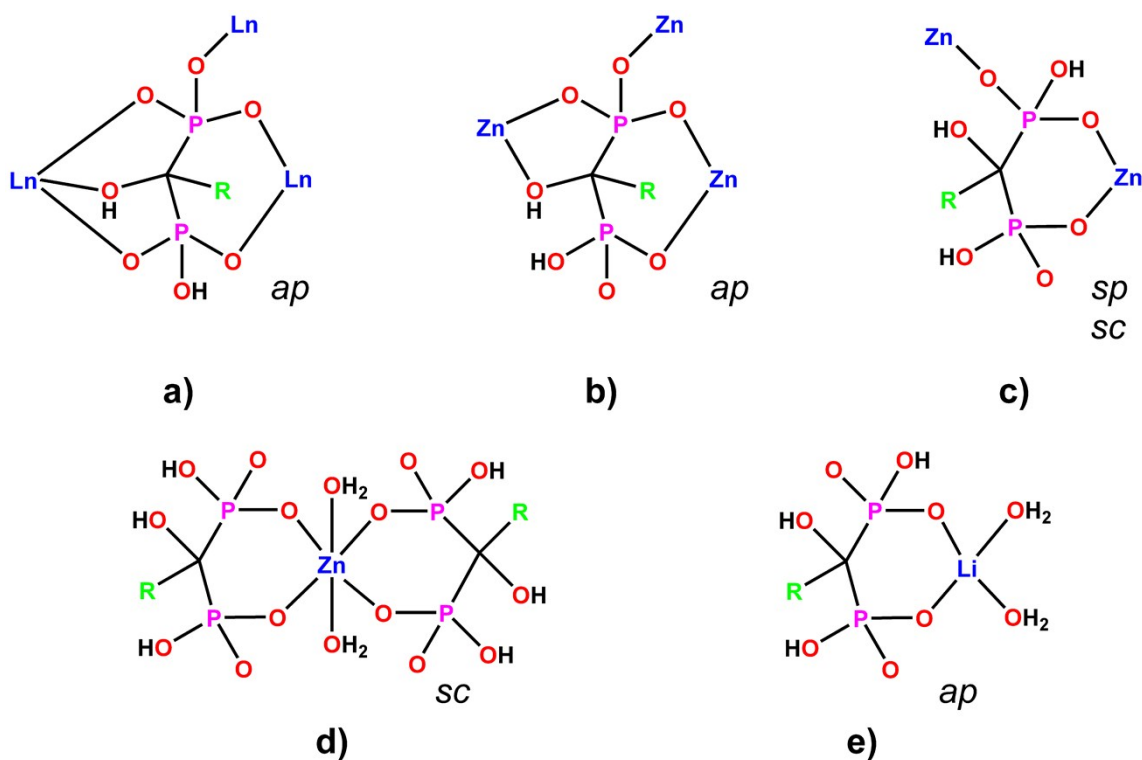


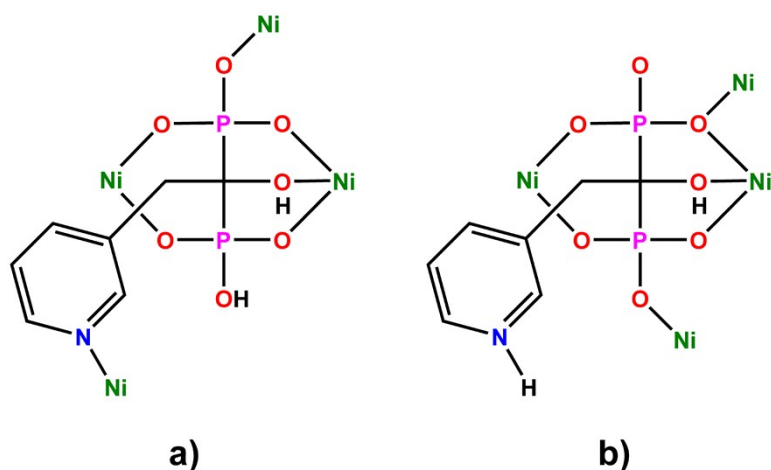
Figure S3. Experimental X-ray powder pattern (black, $T = 298$ K, $\text{Cu-K}\alpha_1$) and simulated powder pattern (red, $T = 100$ K, $\text{Mo-K}\alpha$) based on the results from single-crystal X-ray diffraction for the coordination unit **4a**.



Scheme S1. Ligands coordination modes in $[M_2(H_3L)_4(H_2O)_2] \cdot 2H_2O$ complexes formed by H_3Pam^- ($M = Ni$), H_3Ale^- ($M = Ni, Cu, Co$) and H_3Ner^- ($M = Cd, Mn$).



Scheme S2. Ligand binding modes in (a) $[Ln(HPam)]$, (b) $[Zn(H_2Pam)] \cdot H_2O$, (c) $[Zn(H_3Pam)_2]$ (d) *trans*- $[Zn(H_3Pam)_2] \cdot 2H_2O$ and (e) $Li[(H_3Ale)(H_2O)_2]$ complexes.



Scheme S3. Risedronate coordination modes in (a) $[\text{Ni}_3(\text{HRis})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$ and $[\text{Ni}_3(\text{HRis})_2(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$ and (b) $[\text{Ni}_3(\text{HRis})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$

Table S3. Selected relative energies (ΔE) and torsion angles (τ_1) calculated for conformations and transition states of ligands 1-4.

Conformer	ΔE [kcal/mol]	τ_1 [°]	Conformer	ΔE [kcal/mol]	τ_1 [°]
<i>H₄dmfZol (1)</i>			<i>H₄cbtZol (3)</i>		
<i>sc₁-1</i>	0.00	-59.0	<i>ap₁-3</i>	0.00	-179.0
<i>ap₁-1</i>	0.70	-179.3	<i>sc₁-3</i>	2.40	-60.5
<i>sc₂-1</i>	2.96	+70.2	<i>sc₂-3</i>	6.73	+70.4
<i>ac₁-1</i>	8.52	+110.1	<i>TSsc₁-ap₁-3</i>	11.43	-108.0
<i>TSsc₁-ap₁-1</i>	17.69	-120.0	<i>TSsc₂-ap₁-3</i>	12.59	118.4
<i>TSac₁-ap₁-1</i>	10.59	+120.8	<i>TSsc₁-sc₂-3</i>	12.68	11.4
<i>TSsc₂-ac₁-1</i>	11.61	+99.0			
<i>TSsc₁-sc₂-1</i>	15.71	+1.1			
<i>H₄cppZol (2)</i>			<i>H₄cptZol (4)</i>		
<i>ap₁-2</i>	0.00	+167.8	<i>ap₁-4</i>	0.00	+165.8
<i>sc₁-2</i>	3.88	-53.9	<i>sc₁-4</i>	6.01	+53.5
<i>ap₂-2</i>	3.93	-154.1	<i>ap₂-4</i>	6.73	-166.9
<i>sc₂-2</i>	7.17	55.7	<i>sc₂-4</i>	6.51	+32.5
<i>TSap₁-ap₂-2</i>	6.66	-169.6	<i>sc₃-4</i>	8.62	-27.7
<i>TSap₁-sc₂-2</i>	14.17	+105.4	<i>sc₄-4</i>	9.21	-63.7
<i>TSap₂-sc₁-2</i>	11.54	-103.6	<i>TSsc₁-ap₁-4</i>	16.69	+128.1
<i>TSsc₁-sc₂-2</i>	15.90	-0.3	<i>TSap₁-ap₂-4</i>	18.45	-176.2
			<i>TSsc₄-ap₂-4</i>	19.39	-112.1
			<i>TSsc₃-sc₄-4</i>	11.59	-45.3
			<i>TSsc₁-sc₂-4</i>	6.71	+43.9
			<i>TSsc₂-sc₃-4</i>	12.51	-7.0

Table S4. Experimentally determined and theoretically calculated selected interatomic distances (Å), bond angles (°) and torsion angles (°) for the compound **1a**.

1a					
<i>Bond lengths</i>					
	<i>Exp.</i>	<i>Theory</i>		<i>Exp</i>	<i>Theory</i>
P1A–O1A	1.500(4)	1.536	P1B–O1B	1.499(4)	1.540
P1A–O2A	1.508(5)	1.585	P1B–O2B	1.510(4)	1.589
P1A–O3A	1.568(4)	1.694	P1B–O3B	1.553(4)	1.715
P2A–O4A	1.489(4)	1.537	P2B–O4B	1.490(4)	1.541
P2A–O5A	1.524(4)	1.583	P2B–O5B	1.511(5)	1.604
P2A–O6A	1.568(4)	1.661	P2B–O6B	1.570(4)	1.647
RMSD ^a		0.079			0.093
<i>Bond angles</i>					
N1A–C2A–C1A	107.2(4)	104.9	N1B–C2B–C1B	109.1(4)	106.3
O1A–P1A–O2A	116.6(2)	116.2	O1B–P1B–O2B	114.4(2)	121.7
O1A–P1A–O3A	108.8(2)	112.3	O1B–P1B–O3B	111.7(2)	107.6
O2A–P1A–O3A	109.1(2)	104.9	O2B–P1B–O3B	109.8(2)	104.4
O4A–P2A–O5A	114.5(2)	118.0	O4B–P2B–O5B	114.5(2)	116.4
O4A–P2A–O6A	107.9(2)	111.4	O4B–P2B–O6B	108.8(2)	109.1
O5A–P2A–O6A	108.7(2)	106.4	O5B–P2B–O6B	107.9(2)	107.7
RMSD ^b		3.1			4.0
<i>Torsion angles</i>					
O7A–C1A–C2A–N1A	-54.2(5)	-56.3	O7B–C1B–C2B–N1B	55.0(5)	55.1
P1A–C1A–C2A–N1A	70.7(4)	60.1	P1B–C1B–C2B–N1B	-65.2(4)	-63.9
P2A–C1A–C2A–N1A	-166.9(3)	-171.7	P2B–C1B–C2B–N1B	169.3(3)	173.0
O7A–C1A–C2A–C3A	62.9(6)	59.5	O7B–C1B–C2B–C3B	-61.9(5)	-61.3
P1A–C1A–C2A–C3A	-172.2(4)	175.9	P1B–C1B–C2B–C3B	177.8(3)	179.7
P2A–C1A–C2A–C3A	-49.8(5)	-55.9	P2B–C1B–C2B–C3B	52.4(5)	55.6
O7A–C1A–C2A–C4A	-174.2(5)	-176.4	O7B–C1B–C2B–C4B	175.3(5)	175.0
P1A–C1A–C2A–C4A	-49.3(6)	-60.1	P1B–C1B–C2B–C4B	55.0(5)	56.0
P2A–C1A–C2A–C4A	73.1(5)	68.2	P2B–C1B–C2B–C4B	-70.5(5)	-67.1
RMSD ^b		7.3			2.2

^aRoot mean square deviation of distances (RMSD, in Å) for both ligands. ^bRoot mean square deviation of bond and torsion angles (RMSD, in °) for both ligands.

Table S5. Experimentally determined and theoretically calculated selected interatomic distances (Å), bond angles (°) and torsion angles (°) for the compounds **3a** and **4a**.

	3a		4a	
<i>Bond lengths</i>	<i>Exp.</i>	<i>Theory</i>	<i>Exp.</i>	<i>Theory</i>
P1–O1	1.4991(18)	1.5442	1.498(2)	1.544
P1–O2	1.5087(17)	1.5756	1.505(2)	1.575
P1–O3	1.5628(18)	1.7006	1.564(2)	1.702
P2–O4	1.5011(18)	1.5359	1.498(2)	1.536
P2–O5	1.5259(17)	1.5749	1.520(2)	1.574
P2–O6	1.5593(19)	1.7091	1.566(2)	1.711
RMSD ^a		0.0927		0.093
<i>Bond angles</i>				
N1–C2–C1	108.75(18)	108.61	108.4(2)	107.4
O1–P1–O2	114.69(10)	120.49	114.91(12)	120.53
O1–P1–O3	112.06(10)	108.62	111.84(11)	108.15
O2–P1–O3	111.19(10)	107.78	110.70(12)	107.31
O4–P2–O5	112.19(10)	121.51	112.72(11)	121.48
O4–P2–O6	112.80(10)	108.23	112.40(11)	108.17
O5–P2–O6	108.24(10)	105.45	107.66(12)	105.38
RMSD ^b		4.97		4.74
<i>Torsion angles</i>				
O7–C1–C2–N1	-64.3(2)	-73.2	-65.2(3)	-73.9
P1–C1–C2–N1	53.2(2)	44.8	51.4(3)	43.1
P2–C1–C2–N1	179.21(15)	170.33	178.40(17)	169.45
O7–C1–C2–C3	59.6(3)	50.7	52.9(3)	44.9
P1–C1–C2–C3	177.15(17)	168.80	169.57(19)	161.83
P2–C1–C2–C3	-56.8(3)	-65.7	-63.5(3)	-71.8
O7–C1–C2–C5	167.02(19)	156.84	-	-
P1–C1–C2–C5	-75.5(2)	-85.1	-	-
P2–C1–C2–C5	50.5(3)	40.4	-	-
O7–C1–C2–C6	-	-	171.6(2)	162.9
P1–C1–C2–C6	-	-	-71.7(3)	-80.2
P2–C1–C2–C6	-	-	55.2(3)	46.2
RMSD ^b		9.2		8.5

^aRoot mean square deviation of distances (RMSD, in Å) for compounds **3a** and **4a**. ^bRoot mean square deviation of bond and torsion angles (RMSD, in °) for compounds **3a** and **4a**.

Table S6. Experimentally determined and theoretically calculated selected interatomic distances (Å) and bond angles (°) related to the metal center for the compounds **1a**, **3a** and **4a**.

1a					
<i>Bond lengths (Å)</i>	<i>Exp.</i>	<i>Theory</i>	<i>Bond angles (°)</i>	<i>Exp</i>	<i>Theory</i>
Cu1–O2A	1.941(5)	1.990	O2A–Cu1–O5A	91.02(18)	89.33
Cu1–O5A	1.955(4)	1.942	O2A–Cu1–O5B	88.69(19)	84.10
Cu1–O2B	1.933(4)	1.976	O2A–Cu1–O1W	85.97(15)	102.96
Cu1–O5B	1.961(4)	1.988	O5A–Cu1–O5B	171.26(16)	168.96
Cu1–O1W	2.435(4)	2.439	O5A–Cu1–O1W	101.94(15)	105.64
RMSD ^a		0.003	O2B–Cu1–O2A	174.12(16)	170.22
			O2B–Cu1–O5A	87.33(18)	88.04
			O2B–Cu1–O5B	92.09(18)	96.96
			O2B–Cu1–O1W	99.89(15)	86.82
			O5B–Cu1–O1W	86.76(15)	84.53
			RMSD ^b		7.39

3a			4a	
<i>Bond lengths (Å)</i>	<i>Exp.</i>	<i>Theory</i>	<i>Exp.</i>	<i>Theory</i>
Cu1–O2, O2 ⁱ	1.9103(19)	1.9968	1.910(2)	1.994
Cu1–O5, O5 ⁱ	1.9440(18)	1.9507	1.939(2)	1.951
Cu1–O1W, O1W ⁱ	2.733(3)	2.547	2.725(3)	2.550
RMSD ^a		0.118		0.113
<i>Bond angles (°)</i>				
O2–Cu1–O2 ⁱ	180.0	180.0	180.0	180.0
O2–Cu1–O5 ⁱ	87.18(8)	86.06	87.85(8)	85.82
O2–Cu1–O5	92.82(8)	93.94	92.15(8)	94.17
O2–Cu1–O1W ⁱ	78.05(7)	72.79	80.60(8)	72.76
O5 ⁱ –Cu1–O5	180.0	180.0	180.0	180.0
O5–Cu1–O1W ⁱ	97.83(7)	91.93	97.98(8)	93.68
O1W–Cu1–O2	101.95(7)	107.19	99.40(8)	107.22
O1W–Cu1–O5	82.17(7)	88.09	82.02(8)	86.34
O1W–Cu1–O1W ⁱ	180.0	180.0	180.0	180.0
RMSD ^b		3.76		4.32

^aRoot mean square deviation of distances (RMSD, in Å). ^bRoot mean square deviation of bond angles (RMSD, in °). Symmetry code: (i) $-x+1, -y+1, -z+1$.

Table S7. Selected hydrogen bonds for compound **1a**.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
<i>Compound 1</i>				
O3 <i>A</i> –H3 <i>A</i> ···O1 <i>B</i> ⁱⁱ	0.84	1.81	2.579(5)	151
O6 <i>A</i> –H6 <i>A</i> ···O2 <i>W</i>	0.84	2.10	2.616(6)	120
O7 <i>A</i> –H7 <i>A</i> ···O8 <i>W</i> ⁱⁱⁱ	0.84	1.91	2.695(6)	154
N2 <i>A</i> –H2 <i>A</i> ···O5 <i>A</i> ⁱⁱ	0.88	1.90	2.755(7)	162
O3 <i>B</i> –H3 <i>B</i> ···O1 <i>A</i> ^{iv}	0.84	1.74	2.555(5)	162
O6 <i>B</i> –H6 <i>B</i> ···O6 <i>W</i>	0.84	1.69	2.520(6)	171
O7 <i>B</i> –H7 <i>B</i> ···O3 <i>W</i> ^v	0.84	2.30	2.969(6)	137
N2 <i>B</i> –H2 <i>B</i> ···O5 <i>B</i> ^{vi}	0.88	1.92	2.795(7)	179
O1 <i>W</i> –H1 <i>W</i> ···O2 <i>W</i>	0.84	2.16	2.869(6)	142
O1 <i>W</i> –H2 <i>W</i> ···O3 <i>W</i>	0.84	2.18	2.979(6)	158
O2 <i>W</i> –H3 <i>W</i> ···O7 <i>A</i>	0.84	2.48	3.302(7)	167
O2 <i>W</i> –H4 <i>W</i> ···O5 <i>W</i>	0.84	1.97	2.806(6)	176
O3 <i>W</i> –H5 <i>W</i> ···O4 <i>B</i>	0.84	1.93	2.734(5)	160
O3 <i>W</i> –H6 <i>W</i> ···O3 <i>A</i> ^{iv}	0.84	2.18	2.993(6)	164
O4 <i>W</i> –H7 <i>W</i> ···O7 <i>A</i>	0.84	2.09	2.886(6)	157
O4 <i>W</i> –H8 <i>W</i> ···O6 <i>B</i> ^{vii}	0.84	2.08	2.880(7)	159
O5 <i>W</i> –H9 <i>W</i> ···O9 <i>W</i> ⁱⁱⁱ	0.84	2.08	2.801(9)	144
O5 <i>W</i> –H10 <i>W</i> ···O4 <i>B</i> ^{vii}	0.84	1.96	2.789(6)	168
O6 <i>W</i> –H11 <i>W</i> ···O9 <i>W</i> ^{viii}	0.84	1.83	2.659(6)	169
O6 <i>W</i> –H12 <i>W</i> ···O7 <i>W</i>	0.84	1.95	2.775(7)	169
O7 <i>W</i> –H13 <i>W</i> ···O1 <i>A</i>	0.84	2.11	2.876(7)	151
O7 <i>W</i> –H14 <i>W</i> ···O3 <i>W</i> ^v	0.84	2.09	2.888(7)	159
O8 <i>W</i> –H15 <i>W</i> ···O1 <i>B</i> ^{ix}	0.84	1.99	2.822(6)	169
O8 <i>W</i> –H16 <i>W</i> ···O4 <i>A</i>	0.84	1.88	2.699(5)	163
O9 <i>W</i> –H17 <i>W</i> ···O4 <i>W</i> ^v	0.84	2.03	2.684(7)	134
O9 <i>W</i> –H18 <i>W</i> ···O4 <i>A</i>	0.84	1.98	2.740(6)	149
C3 <i>A</i> –H3 <i>AC</i> ···O4 <i>W</i>	0.98	2.38	3.357(7)	171
C4 <i>A</i> –H4 <i>AA</i> ···O2 <i>W</i> ^{ix}	0.98	2.48	3.362(8)	149
C4 <i>A</i> –H4 <i>AB</i> ···O1 <i>A</i>	0.98	2.57	3.106(7)	114
C4 <i>A</i> –H4 <i>AB</i> ···O3 <i>B</i> ^{ix}	0.98	2.48	3.390(7)	154
C4 <i>A</i> –H4 <i>AC</i> ···O4 <i>A</i>	0.98	2.37	3.131(8)	133
C21 <i>A</i> –H21 <i>A</i> ···O1 <i>W</i> ^{ix}	0.95	2.58	3.473(6)	156
C4 <i>B</i> –H4 <i>BB</i> ···O4 <i>B</i>	0.98	2.35	3.108(8)	133
C4 <i>B</i> –H4 <i>BC</i> ···O3 <i>B</i>	0.98	2.57	3.159(7)	119
C21 <i>B</i> –H21 <i>B</i> ···O7 <i>W</i> ^{iv}	0.95	2.50	3.442(7)	171
C41 <i>B</i> –H41 <i>B</i> ···O6 <i>W</i> ^{vi}	0.95	2.55	3.251(8)	131

Symmetry codes: (ii) $x+1, y+1, z$; (iii) $x+1, y, z$; (iv) $x, y-1, z$; (v) $x-1, y, z$; (vi) $x-1, y-1, z$; (vii) $x, y, z-1$; (viii) $x, y, z+1$; (ix) $x, y+1, z$.

Table S8. Selected hydrogen bonds for compounds **3a** and **4a**.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
<i>Compound 3a</i>				
O3–H3···O5 ^v	0.84	1.84	2.666(3)	168
O6–H6···O4 ^x	0.84	1.68	2.521(3)	177
O7–H7···O1 ^W	0.84	2.22	3.029(3)	161
N2–H2 ^N ···O1 ^{xi}	0.88	1.77	2.614(3)	159
O1 ^W –H1 ^W ···O6 ⁱ	0.84	2.40	3.225(3)	169
O1 ^W –H2 ^W ···O1 ⁱⁱⁱ	0.84	1.99	2.810(3)	164
C3–H3 ^A ···O4	0.99	2.31	3.067(3)	132
C41–H41···O7 ^v	0.95	2.58	3.155(3)	120
C51–H51···O4 ^v	0.95	2.31	3.261(3)	176
<i>Compound 4a</i>				
O3–H3···O5 ^v	0.84	1.88	2.689(3)	161
O6–H6···O4 ^x	0.84	1.72	2.552(3)	174
O7–H7···O1 ^W	0.84	2.23	3.053(3)	166
N2–H2 ^N ···O1 ^{xi}	0.88	1.81	2.646(4)	158
O1 ^W –H1 ^W ···O6 ⁱ	0.84	2.48	3.218(3)	147
O1 ^W –H2 ^W ···O1 ⁱⁱⁱ	0.84	1.98	2.808(3)	169
C3–H3 ^B ···O4	0.99	2.25	3.056(4)	138
C6–H6 ^B ···O4 ^x	0.99	2.53	3.501(4)	169
C41–H41···O7 ^v	0.95	2.49	3.118(4)	124
C51–H51···O4 ^v	0.95	2.27	3.216(4)	177

Symmetry codes: (x) $-x+1, -y+1, -z+2$; (xi) $-x, -y, -z+1$.

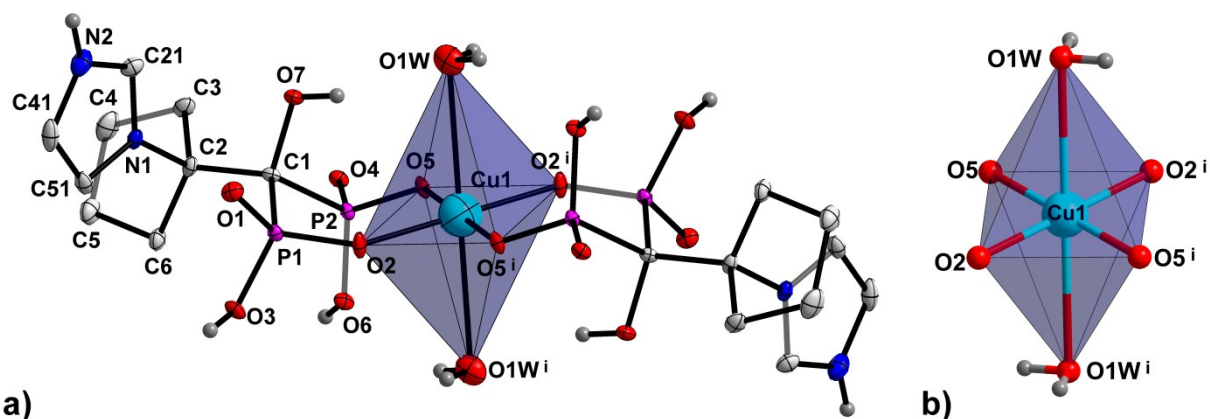


Figure S4. (a) The discrete coordination unit of complex **4a** with the atom-numbering scheme. Displacement ellipsoids except Cu1 atom are drawn at 50% probability level. All C-bond H-atoms are omitted for clarity. (b) Coordination environment of Cu1 center. Symmetry code (i) $-x+1, -y+1, -z+1$.

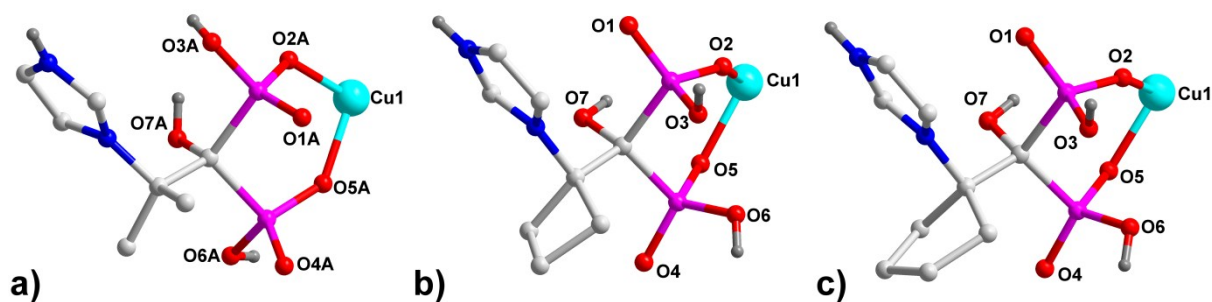


Figure S5. Coordination modes of (a) $\text{H}_3\text{dmtZol}^-$ in **1a**, (b) $\text{H}_3\text{cbtZol}^-$ in **3a** and (c) $\text{H}_3\text{cptZol}^-$ in **4a**. All C-bond H-atoms are omitted for clarity

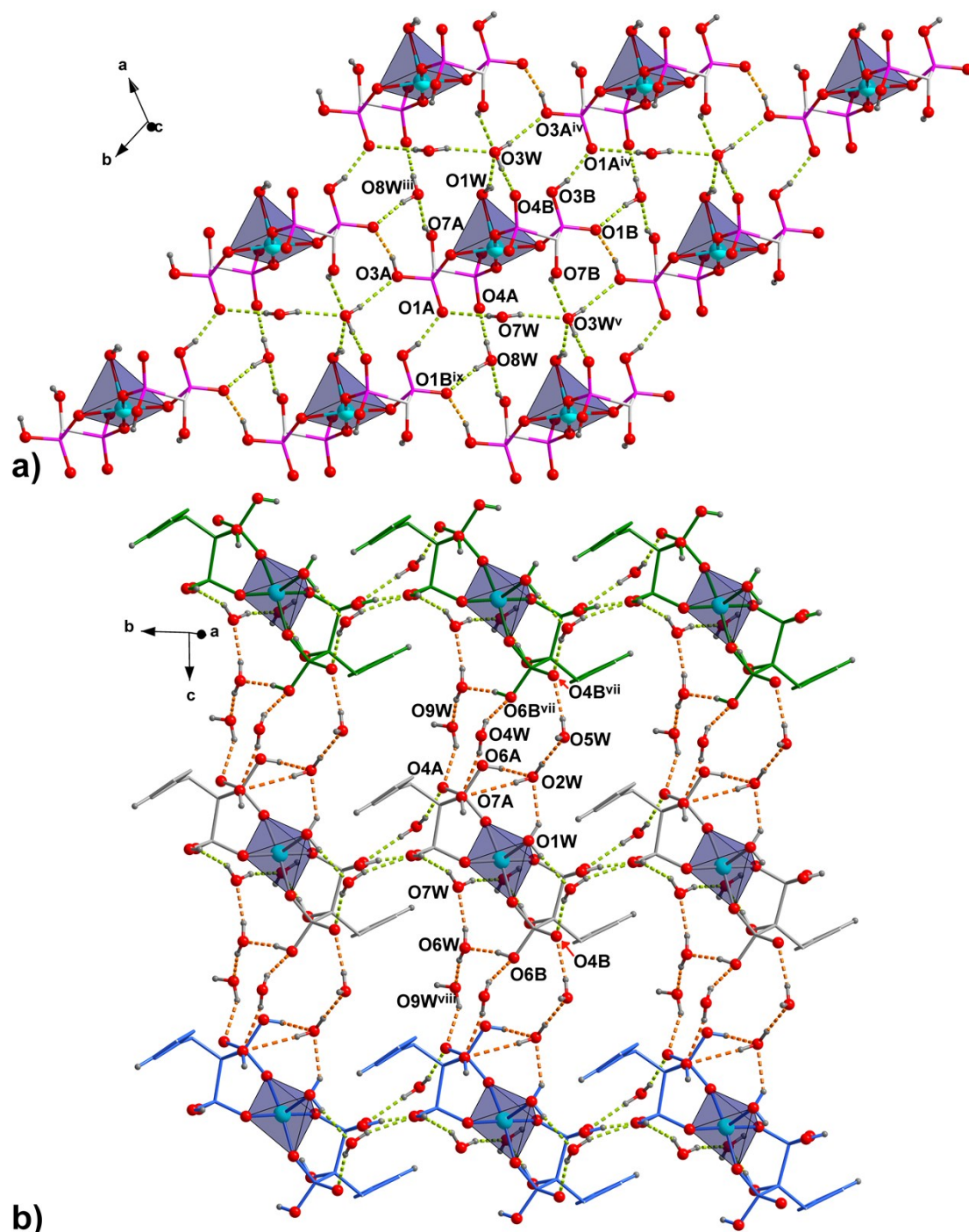


Figure S6. The crystal packing of **1a**. (a) The role of lattice water molecules in stabilization of 2D layer. (c) Assembling of neighbouring layers (shown in green, grey and light blue) into 3D supramolecular network through O–H \cdots O interaction mediated by lattice water molecules. All C-bounded H-atoms, methyl groups, imidazole ring (picture a) and lattice water molecules not involved in arrangement of 2D or 3D structures are omitted for clarity. The intra- and interlayer hydrogen bond network is shown as lime and orange dashed lines, respectively. Symmetry codes are given in Table S7.

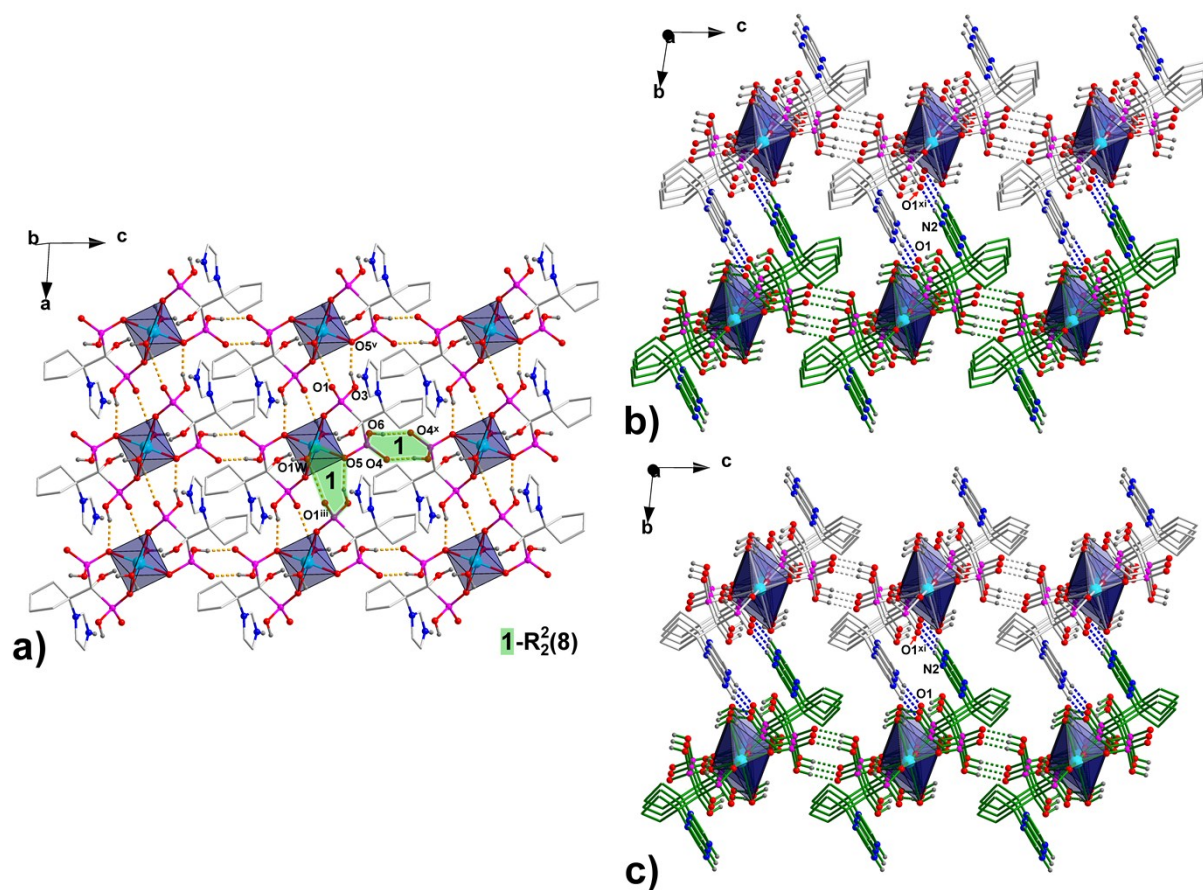


Figure S7. (a) The 2D layer of **4a** generated by means of O–H···O hydrogen bonds shown as light orange dashed lines. (b) and (c) Connection of neighbouring layers (shown in grey and green) into 3D supramolecular network through N–H···O interactions (blue dashed lines) in **4a** and **3a**, respectively. All C-bounded H-atoms are omitted for clarity. Symmetry codes are given in Table S8.

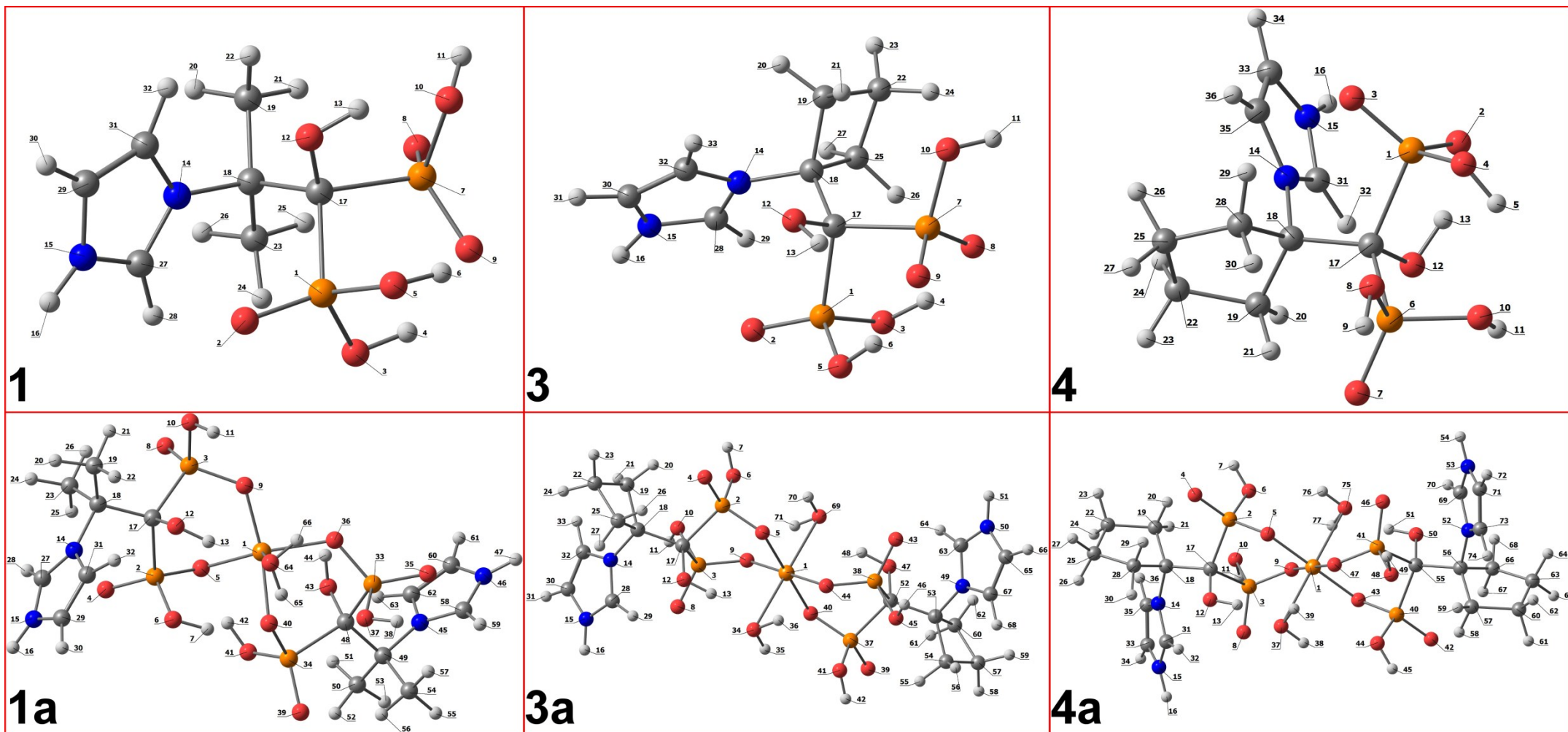


Figure S8. Optimized molecular geometry and the atom-numbering scheme of ligands 1, 3 and 4 and related complexes 1a, 3a and 4a.

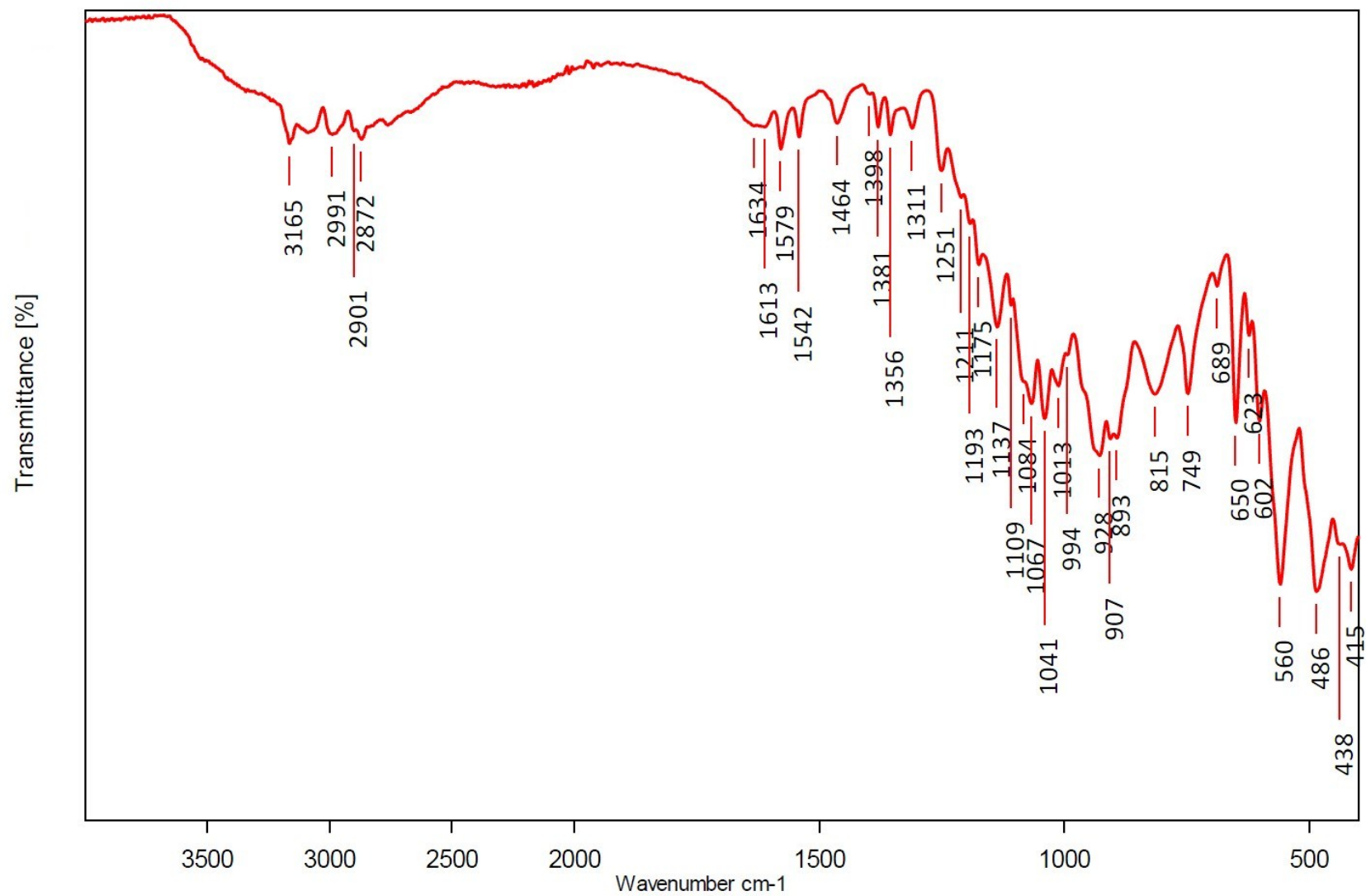


Figure S9. Experimental IR spectrum of complex **1a**.

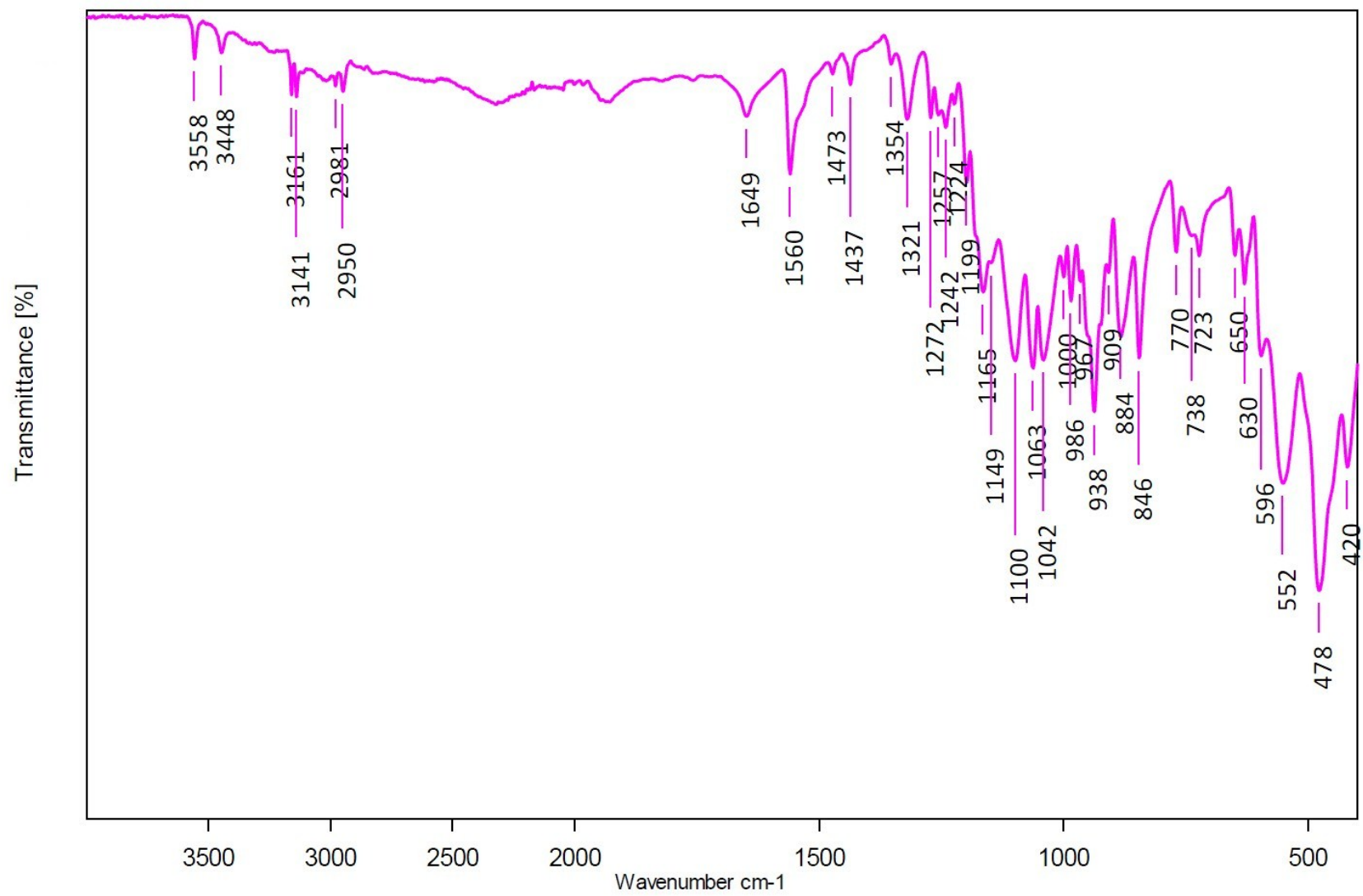


Figure S10. Experimental IR spectrum of complex **3a**.

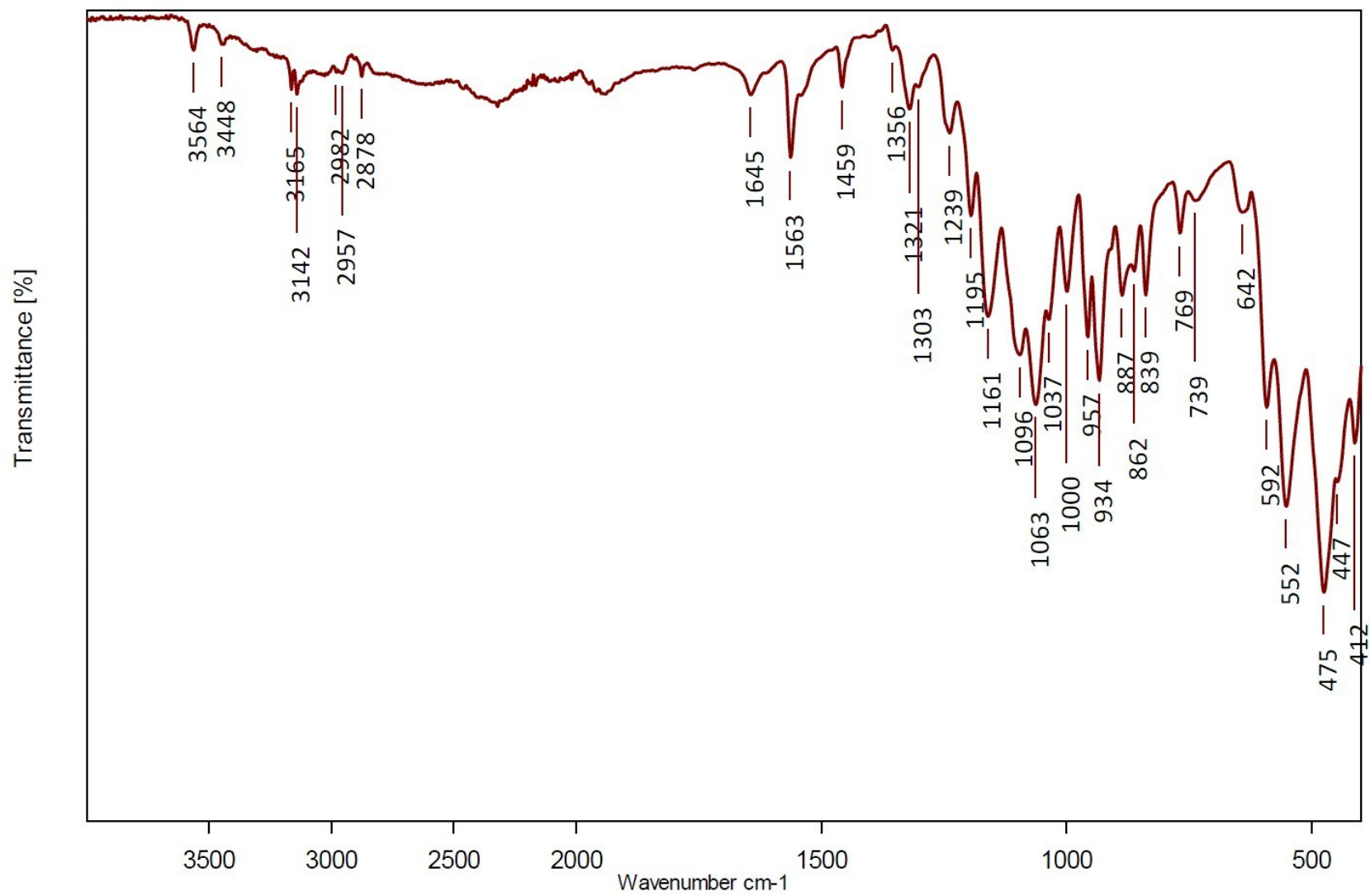


Figure S11. Experimental IR spectrum of complex **4a**.

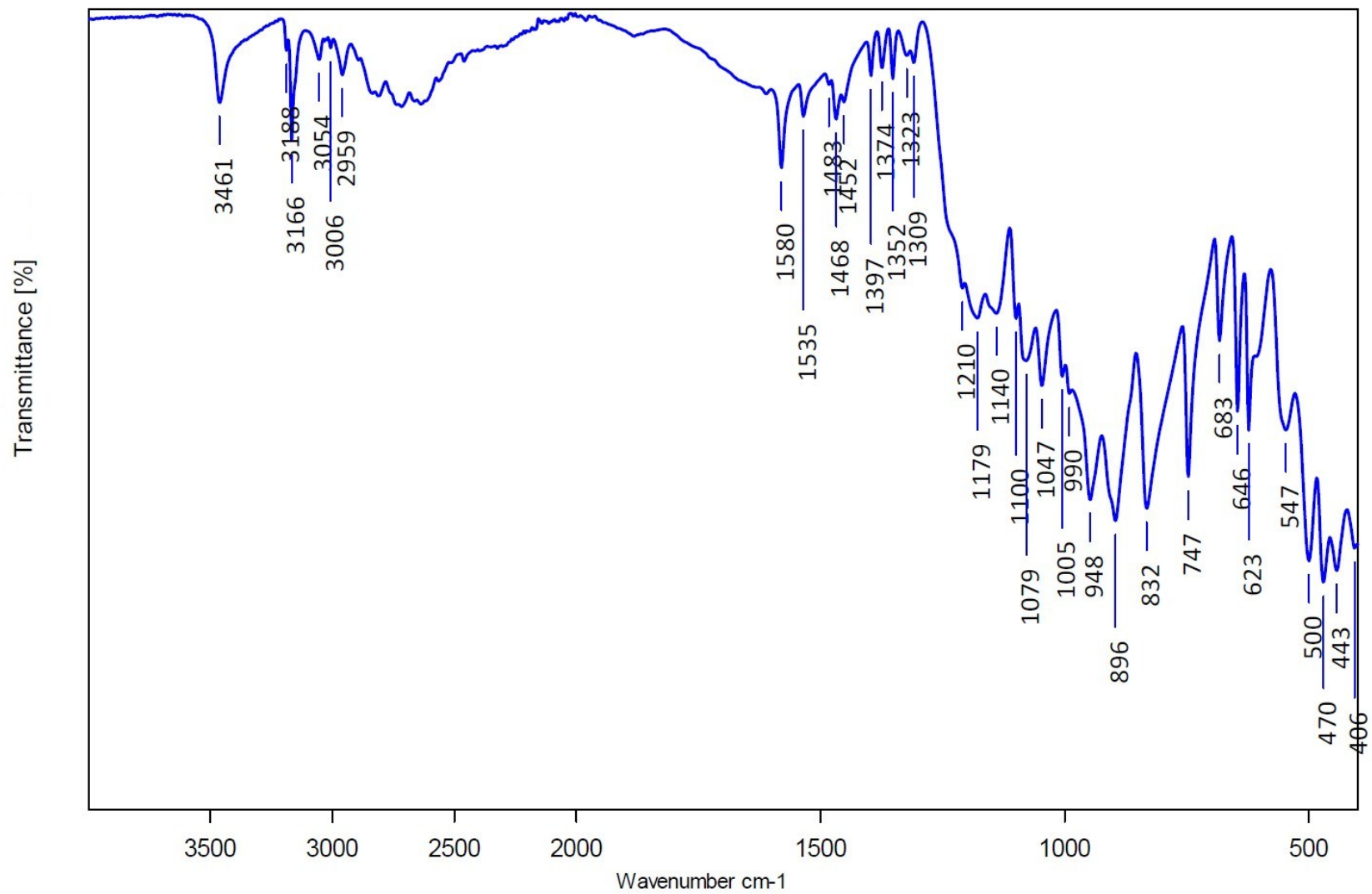


Figure S12. Experimental IR spectrum of ligand **1**.

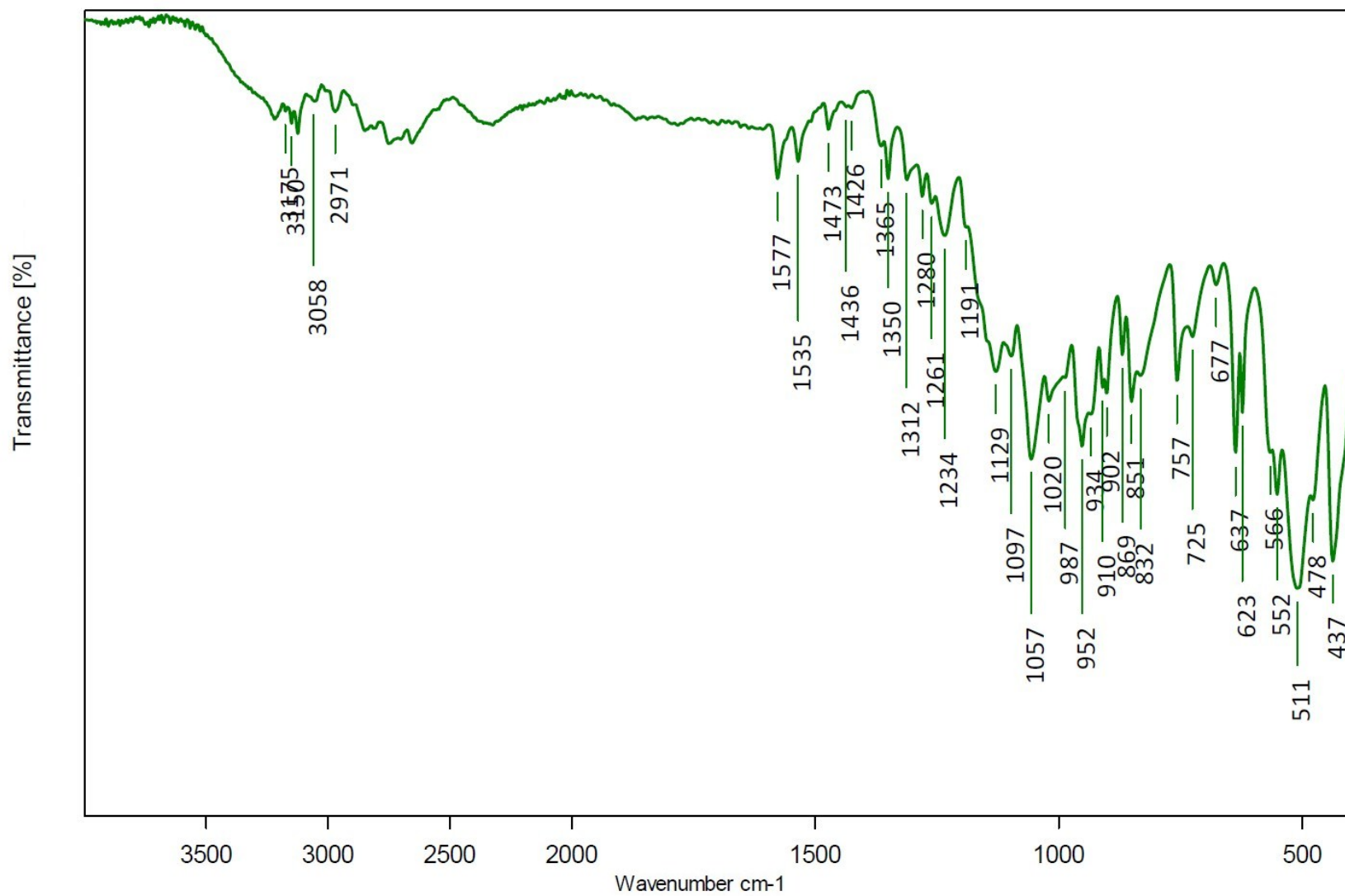


Figure S13. Experimental IR spectrum of ligand 3·H₂O.

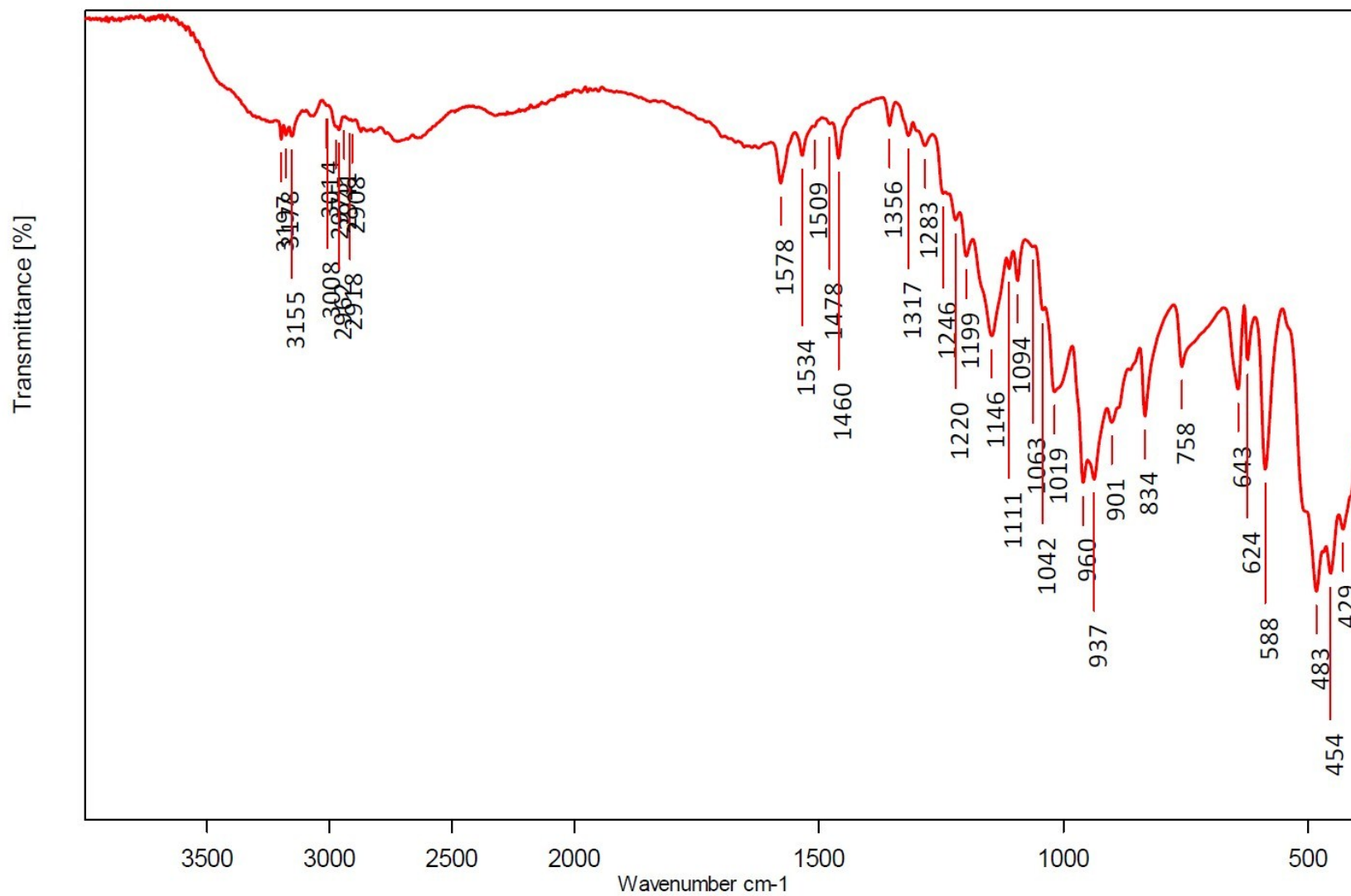


Figure S14. Experimental IR spectrum of ligand $4 \cdot 4\text{H}_2\text{O}$.

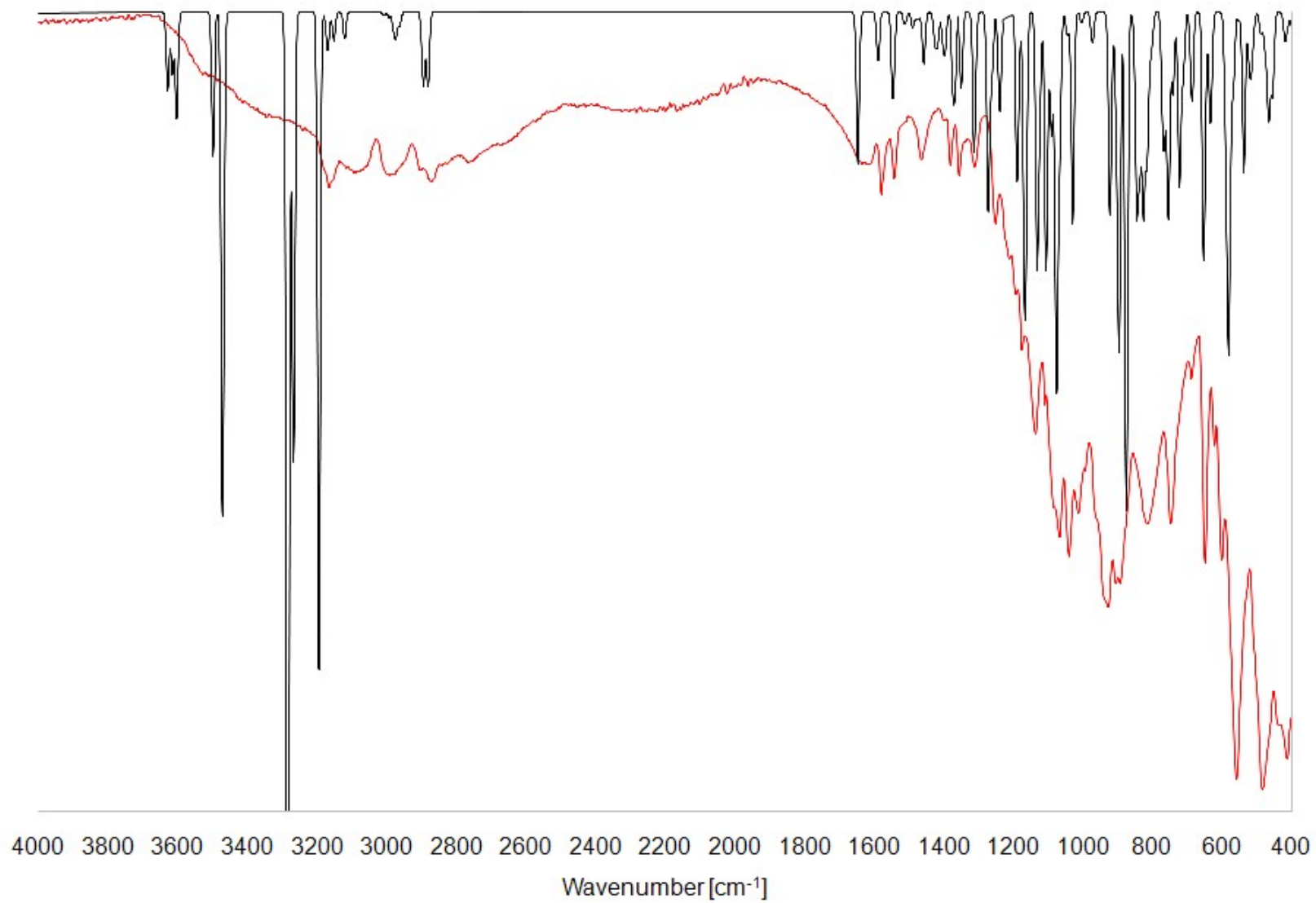


Figure S15. Comparison of experimental and the corresponding theoretical FT-IR spectrum (red and black line, respectively) of complex **1a**.

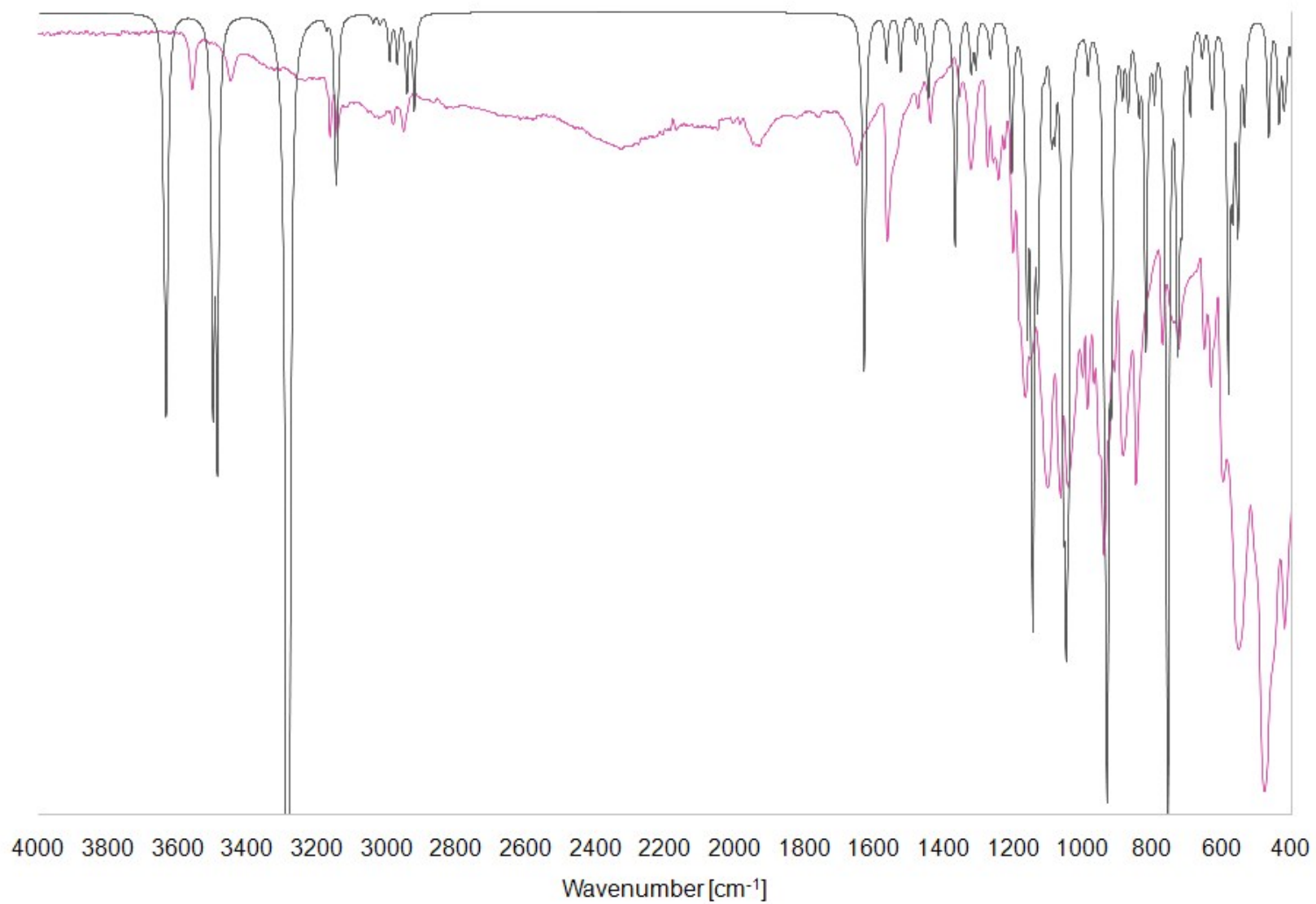


Figure S16. Comparison of experimental and the corresponding theoretical FT-IR spectrum (pink and black line, respectively) of complex **3a**.

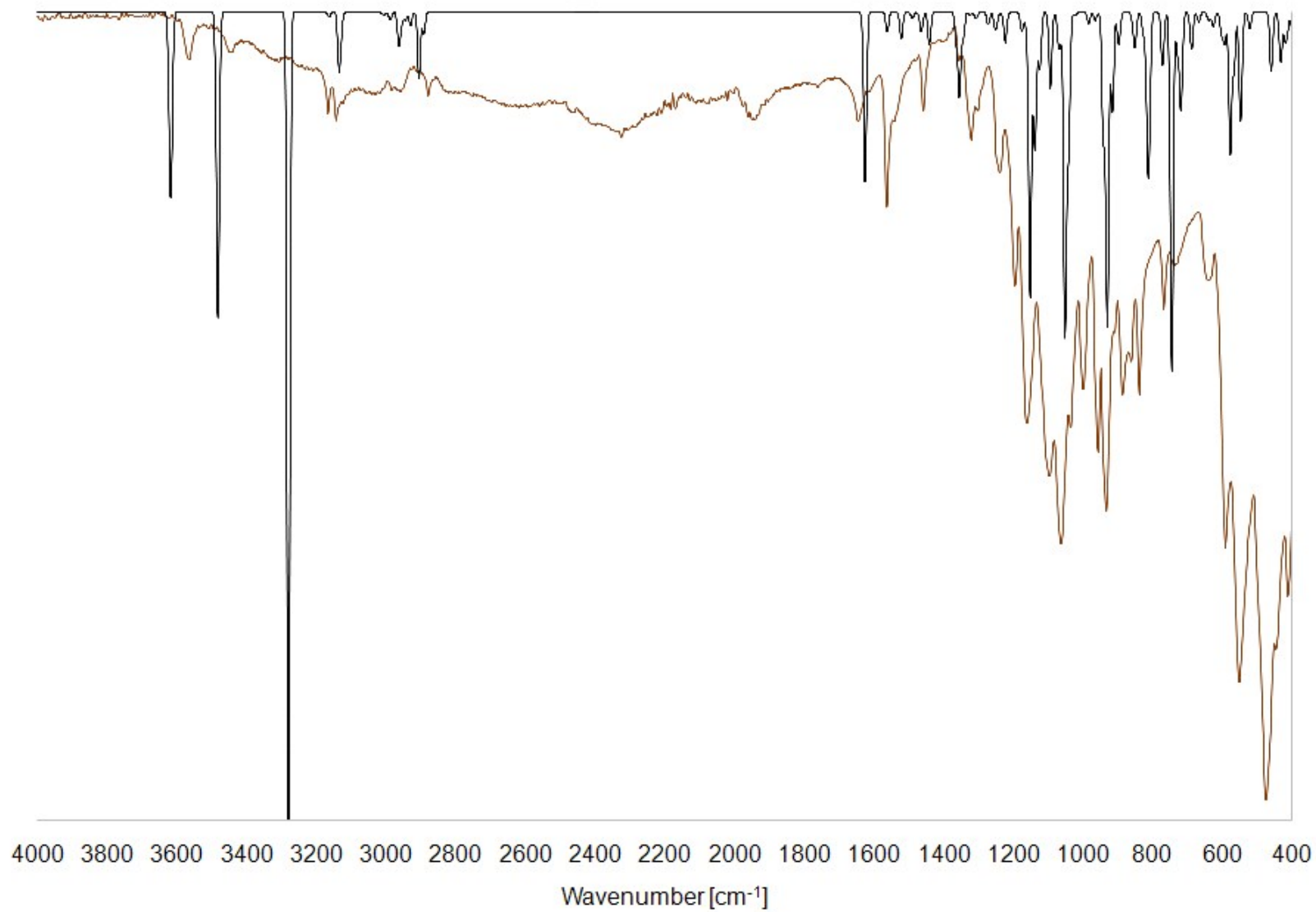


Figure S17. Comparison of experimental and the corresponding theoretical FT-IR spectrum (brown and black line, respectively) of complex **4a**.

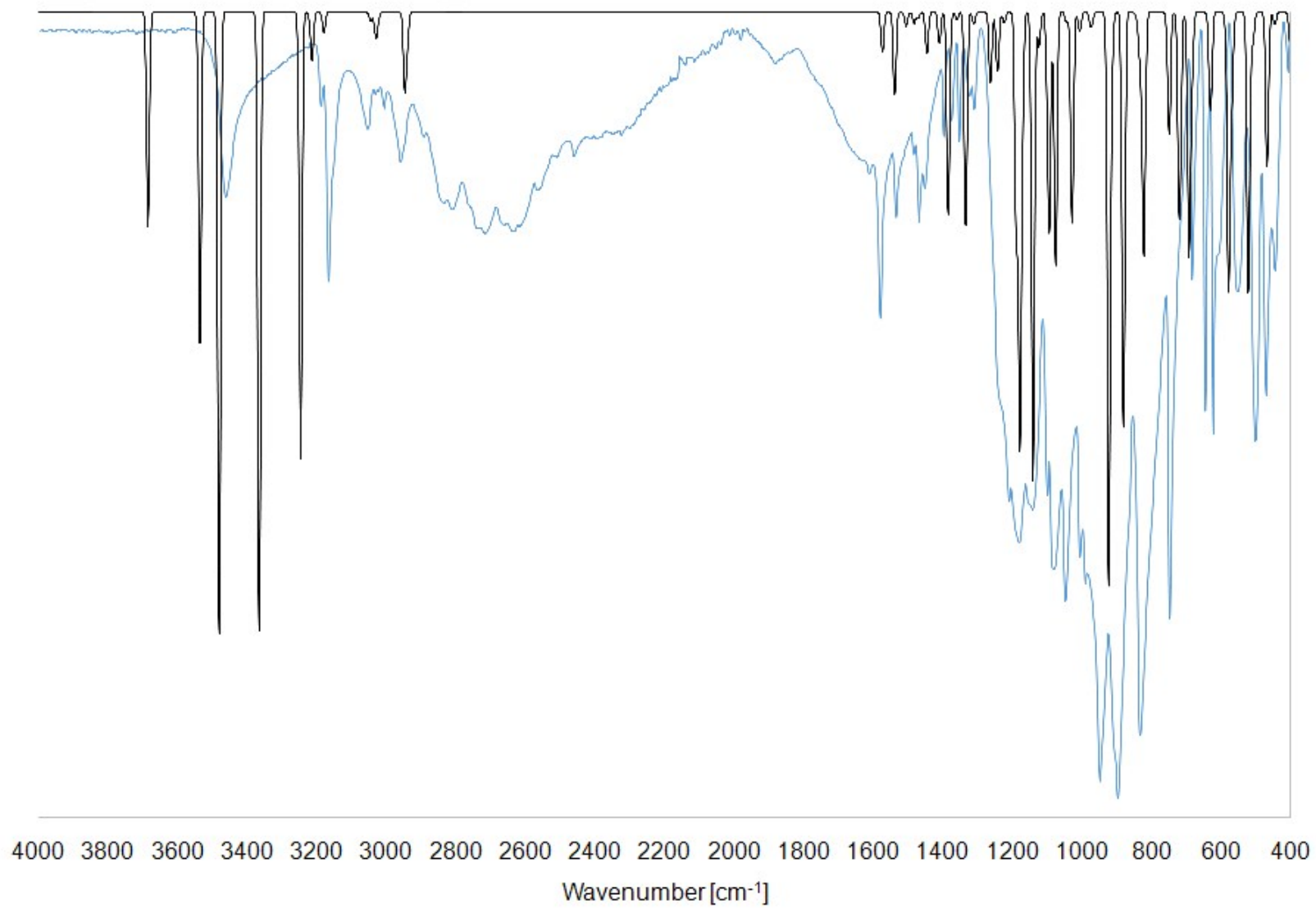


Figure S18. Comparison of experimental and the corresponding theoretical FT-IR spectrum (blue and black line, respectively) of ligand **1**.

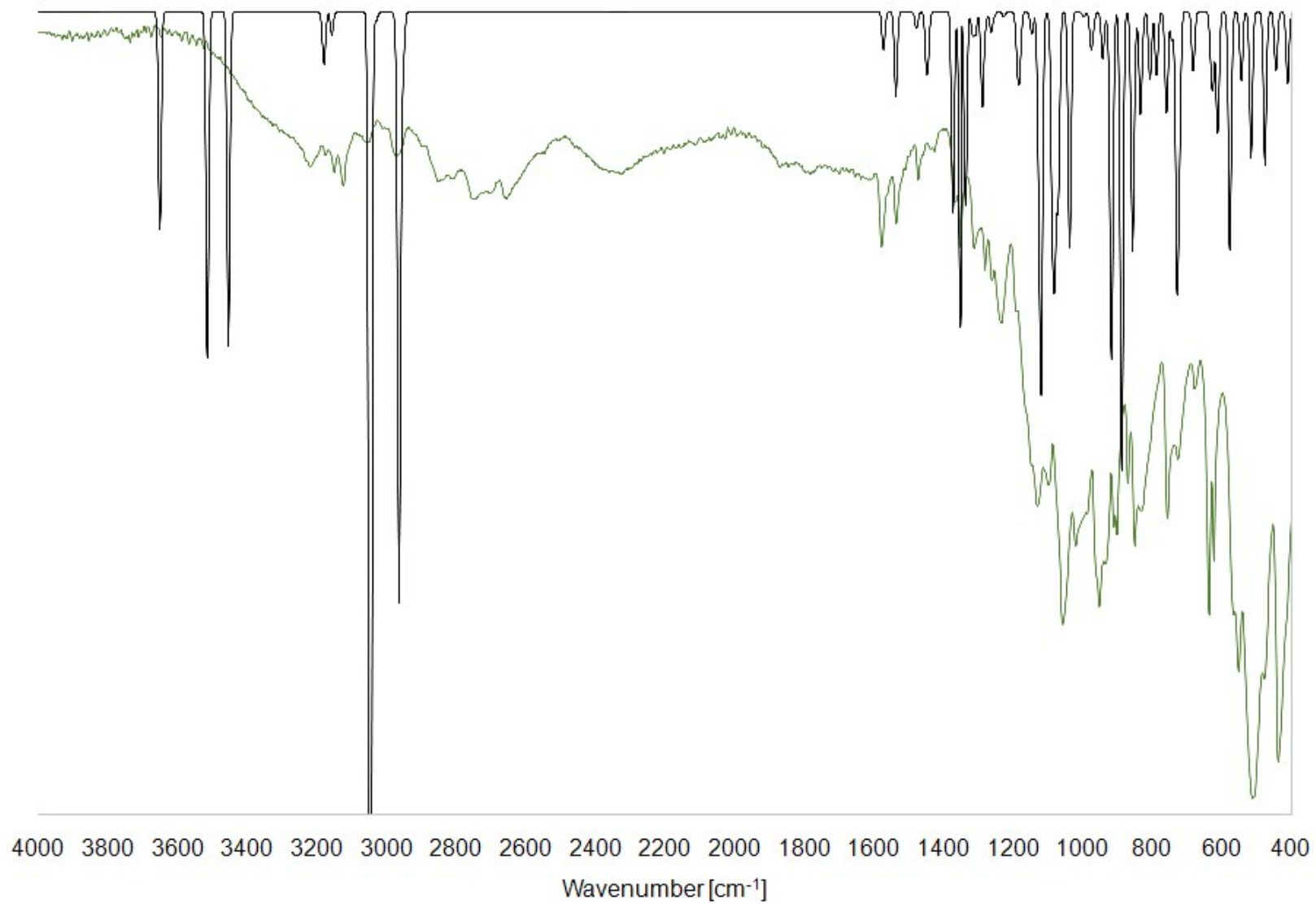


Figure S19. Comparison of experimental and the corresponding theoretical FT-IR spectrum (green and black line, respectively) of ligand **3**.

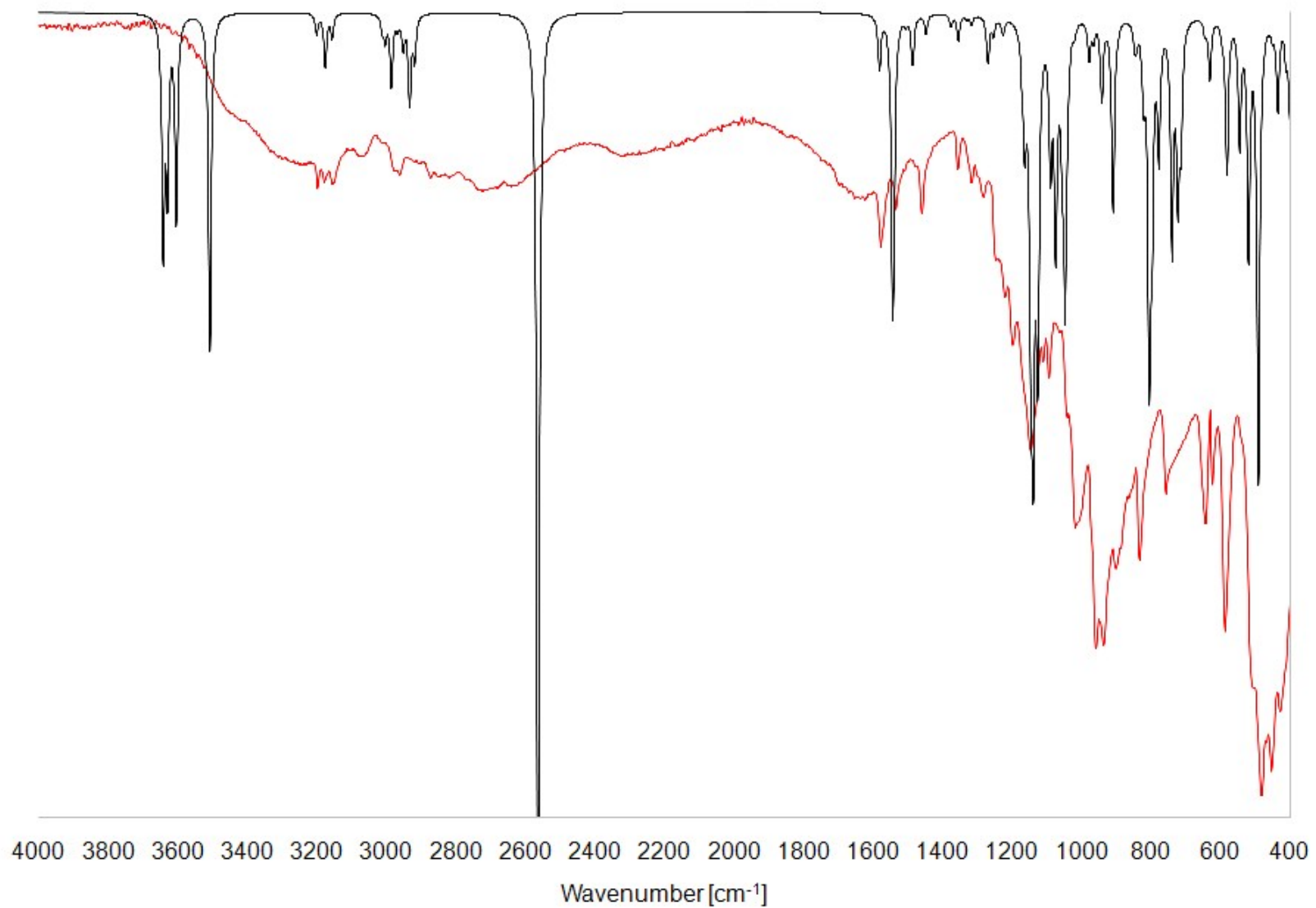


Figure S20. Comparison of experimental and the corresponding theoretical FT-IR spectrum (red and black line, respectively) of ligand **4**.

Table S9. Frequencies of theoretical and experimental IR bands and their vibrational assignments of complex **1a**.

No.	Calcd ^a ν [cm ⁻¹]	Exp. ν [cm ⁻¹]	General assignment ^{b,c}	Functional group	PED ^d
1.	3629	3650-3200 br	v _{as} (O–H)	H ₂ O	v(O64–H66)(62), v(O64–H65)(6)
2.	3615		v(O–H)	phosphonate PO–H	v(O10–H11)(75)
3.	3603				v(O37–H38)(100)
4.	3499		v _s (O–H)	H ₂ O	v(O64–H65)(54), v(O64–H66)(6)
5.	3472		v(N–H)	imidazole	v(N15–H16)(86), v(O43–H44)(9)
6.	3469				v(N46–H47)(94)
7.	3284		v(O–H)	hydroxyl CO–H	v(O12–H13)(58), v(O41–H42)(5)
8.	3267		v(O–H)	phosphonate PO–H	v(O41–H42)(66), v(O12–H13)(5)
9.	3194				v(O6–H7)(62)
10.	3171	3165 br	v(C–H)	imidazole	v(C58–H59)(98)
11.	3168				v(C27–H28)(97)
12.	3152				v(C31–H32)(87), v(C29–H30)(9)
13.	3151	3088 br	v(C–H)	imidazole	v(C62–H63)(88), v(C60–H61)(9)
14.	3121				v(C29–H30)(89), v(C31–H32)(10)
15.	3119				v(C60–H61)(89), v(C62–H63)(10)
16.	3007	2991 br	v _{as} (C–H)	–CH ₃	v(C19–H21)(70), v(C19–H22)(26)
17.	2994				v(C23–H26)(59), v(C23–H25)(38)
18.	2991				v(C50–H52)(50), v(C50–H51)(49)
19.	2980				v(C19–H22)(52), v(C19–H20)(33), v(C19–H21)(13)
20.	2976				v(C50–H53)(31), v(C50–H51)(24), v(C54–H56)(19), v(C50–H52)(17)
21.	2973				v(C54–H56)(46), v(C54–H57)(23), v(C50–H53)(12), v(C50–H52)(12)
22.	2972				v(C23–H25)(41), v(C23–H24)(32), v(C23–H26)(25)
23.	2962				v(C54–H55)(50), v(C54–H57)(42), v(C54–H56)(7)
24.	2896				2901
25.	2892	v(C50–H53)(54), v(C50–H51)(22), v(C50–H52)(20)			
26.	2883	2872	v _s (C–H)	–CH ₃	v(C23–H24)(65), v(C23–H25)(17), v(C23–H26)(13)
27.	2880				v(C54–H55)(45), v(C54–H57)(26), v(C54–H56)(24)
28.	1647	1634, 1613 br	ρ _s (H ₂ O)	H ₂ O	ρ(H65–O64–H66)(31)
29.	1589	1579	v(C=C), v(C–N), δ(im)	imidazole	v(C60–C62)(26), δ(H47–N46–C60)(17), δ(H47–N46–C58)(13), v(C58–N45)(9)
30.	1588				δ(N14–C31–C32)(44), v(C29–C31)(19), δ(H16–N15–C29)(6), δ(N15–C29–H30)(5)
31.	1547	1542	v(C=N), v(C–N), δ(im)	imidazole	δ(H47–N46–C60)(61), v(C58–N46)(13), v(C58–N45)(7)
32.	1544				δ(H16–N15–C29)(36), v(C27–N15)(20), v(C27–N14)(9), δ(N15–C29–H30)(8)

33.	1514	1503-1479 br	$\delta_{as}(\text{CH}_3)$	-CH ₃	$\delta(\text{H24-C23-H25})(26)$, $\delta(\text{H25-C23-H26})(26)$, $\delta(\text{H21-C19-H22})(13)$, $\delta(\text{N14-C31-H32})(9)$
34.	1510				$\delta(\text{H56-C54-H57})(34)$, $\delta(\text{H51-C50-H52})(17)$, $\delta(\text{H55-C54-H56})(9)$, $\delta(\text{H47-N46-C60})(8)$
35.	1489				$\delta(\text{H21-C19-H22})(39)$, $\delta(\text{H24-C23-H25})(18)$, $\delta(\text{H20-C19-H21})(11)$, $\delta(\text{N14-C31-H32})(8)$ $\delta(\text{H51-C50-H52})(30)$, $\delta(\text{H52-C50-H53})(27)$, $\delta(\text{H56-C54-H57})(12)$, $\delta(\text{H55-C54-H57})(8)$
36.	1459	1464	$\nu(\text{C=N})$, $\nu(\text{C-N})$, $\nu(\text{C=C})$	imidazole	$\nu(\text{C60-N46})(23)$, $\nu(\text{C58-N46})(21)$, $\nu(\text{C60-C62})(15)$, $\delta(\text{H55-C54-H56})(5)$
37.	1456				$\nu(\text{C27-N15})(28)$, $\nu(\text{C29-N15})(23)$, $\nu(\text{C29-C31})(19)$
38.	1425	1427-1416 br	$\delta_s(\text{CH}_3)$	-CH ₃	$\delta(\text{C18-C23-H26})(13)$, $\delta(\text{H24-C23-H26})(11)$, $\delta(\text{H20-C19-H21})(9)$, $\delta(\text{C18-C23-H25})(9)$
39.	1417				$\delta(\text{H55-C54-H56})(11)$, $\delta(\text{C49-C50-H52})(11)$, $\delta(\text{H52-C50-H53})(11)$, $\delta(\text{C49-C54-H56})(9)$
40.	1403	1398	$\delta_s(\text{CH}_3)$	-CH ₃	$\delta(\text{H20-C19-H22})(14)$, $\delta(\text{C18-C19-H20})(11)$, $\delta(\text{C18-C19-H21})(11)$, $\delta(\text{C18-C19-H22})(9)$
41.	1396				$\delta(\text{C49-C54-H56})(12)$, $\delta(\text{C49-C50-H52})(8)$, $\delta(\text{H55-C54-H56})(8)$, $\delta(\text{H51-C50-H52})(7)$
42.	1374				1381
43.	1371	$\nu(\text{C=N})$, $\nu(\text{C-N})$	$\nu(\text{C62-N45})(22)$, $\nu(\text{C58-N45})(15)$, $\delta(\text{H61-C60-C62})(7)$, $\delta(\text{C60-C62-H63})(7)$		
44.	1350	1356	$\delta(\text{COH})$		$\delta(\text{C48-O43-H44})(71)$, $\nu(\text{C48-C49})(8)$
45.	1313	1311	$\delta(\text{POH})$	phosphonate P-O-H	$\delta(\text{P2-O6-H7})(24)$, $\delta(\text{P34-O41-H42})(17)$
46.	1273	1251			$\delta(\text{P34-O41-H42})(38)$, $\delta(\text{P2-O6-H7})(13)$
47.	1241	1211	$\rho_r(\text{CH}_3)$	-CH ₃	$\nu(\text{C48-C49})(17)$, $\delta(\text{C49-C50-H53})(8)$, $\delta(\text{C49-C54-H55})(7)$, $\nu(\text{C49-N45})(5)$
48.	1237				$\nu(\text{C17-C18})(15)$, $\delta(\text{C18-C23-H24})(8)$, $\delta(\text{C18-C19-H20})(6)$, $\nu(\text{C18-C19})(5)$
49.	1190	1193	$\rho_r(\text{CH}_3)$	-CH ₃	$\delta(\text{C49-C50-H52})(11)$, $\delta(\text{C49-C54-H56})(11)$, $\nu(\text{C49-N45})(5)$, $\delta(\text{C49-C54-H57})(4)$
50.	1187				$\delta(\text{C18-C23-H26})(12)$, $\delta(\text{C18-C19-H21})(12)$, $\nu(\text{C31-N14})(6)$, $\delta(\text{C18-C19-H22})(4)$
51.	1165				1175
52.	1132	1137	$\delta(\text{P33-O37-H38})(29)$, $\nu(\text{P33-O35})(20)$, $\delta(\text{H47-N46-C60})(18)$, $\delta(\text{H47-N46-C58})(10)$		
53.	1108	1109	$\nu(\text{C-O})$	hydroxyl C-OH	$\nu(\text{C17-O12})(31)$, $\delta(\text{C29-C31-H32})(11)$, $\nu(\text{P34-O39})(6)$
54.	1106		$\nu(\text{P=O})$	phosphonate P=O	$\nu(\text{P34-O39})(71)$
55.	1093	1084	$\nu(\text{C-N})$	imidazole	$\nu(\text{C60-N46})(44)$, $\delta(\text{N45-C62-H63})(7)$, $\delta(\text{N46-C58-H59})(6)$, $\delta(\text{C60-C62-H63})(5)$
56.	1089				$\nu(\text{C29-N15})(49)$, $\delta(\text{C27-N14-C31})(12)$, $\delta(\text{N15-C27-H28})(6)$, $\delta(\text{N14-C27-H28})(6)$
57.	1078	1067	$\nu(\text{C-O})$	hydroxyl C-OH	$\nu(\text{C48-O43})(44)$, $\delta(\text{H47-N46-C58})(10)$
58.	1076		$\nu(\text{P=O})$	phosphonate P=O	$\nu(\text{P2-O4})(71)$, $\delta(\text{C29-C31-H32})(14)$, $\delta(\text{N14-C31-H32})(11)$
59.	1030	1041	$\nu(\text{P=O})$, $\delta(\text{POH})$	phosphonate P=O	$\nu(\text{P33-O35})(47)$, $\delta(\text{P33-O37-H38})(28)$, $\nu(\text{P33-O36})(5)$
60.	1004	1013	$\delta_{\text{ring}}(\text{im})$	imidazole	$\delta(\text{H47-N46-C60})(18)$, $\delta(\text{N46-C60-H61})(9)$, $\delta(\text{N45-C58-N46})(8)$, $\delta(\text{C58-N46-C60})(7)$ $\delta(\text{C29-C31-H32})(15)$, $\delta(\text{C27-N14-C31})(11)$, $\delta(\text{N15-C29-H30})(11)$, $\delta(\text{N14-C31-C29})(7)$
61.	975	994	$\rho_r(\text{CH}_3)$	-CH ₃	$\nu(\text{C48-C49})(31)$, $\delta(\text{C49-C54-H55})(8)$, $\nu(\text{C49-C54})(7)$
62.	973				$\nu(\text{C17-C18})(22)$, $\nu(\text{C18-C19})(12)$, $\delta(\text{C18-C23-H25})(8)$, $\delta(\text{C18-C23-H24})(8)$
63.	971				$\delta(\text{C18-C19-H22})(19)$, $\nu(\text{C18-C23})(17)$, $\delta(\text{C18-C23-H25})(7)$, $\delta(\text{C18-C23-H26})(5)$
64.	969				$\delta(\text{C49-C50-H51})(18)$, $\delta(\text{C49-C54-H57})(18)$, $\nu(\text{C49-C54})(14)$, $\nu(\text{C49-C50})(12)$
65.	926	928	$\delta_{\text{ring}}(\text{im})$	imidazole	$\delta(\text{C27-N15-C29})(20)$, $\delta(\text{H16-N15-C27})(18)$, $\delta(\text{N15-C29-C31})(15)$, $\delta(\text{N14-C31-C29})(14)$ $\delta(\text{C58-N46-C60})(28)$, $\delta(\text{H47-N46-C58})(24)$, $\delta(\text{H47-N46-C60})(22)$, $\delta(\text{N46-C60-C62})(5)$

66.	906	907	v(P-O)	phosphonate P-O	v(P33-O36)(17), δ (C29-C31-H32)(13), v(C17-C18)(9), v(P33-O35)(8)
67.	896	893			v(P34-O40)(23), v(P2-O5)(10), v(P34-O41)(7)
68.	876	- br			v(P3-O9)(20), v(P33-O36)(11), v(P2-O5)(9)
69.	837	815 br	v(skel)	skeletal vib.	v(C18-C19)(11), v(P2-C17)(11)
70.	827				v(C49-C50)(9), v(P33-C48)(8)
71.	809		γ (im), τ (im)	imidazole	γ (H28-C27,N14,N15)(68), τ (N14-C27-N15-C29)(12), γ (H30-C29,N15,C31)(4) γ (H59-C58,N45,N46)(64), τ (N45-C58-N46-C60)(14), γ (H61-C60,N46,C62)(6), τ (C48-C49-N45-C58)(4)
73.	771	749 br	v(P-O)	phosphonate P-OH	v(P34-O41)(38), v(P33-O37)(12)
74.	764				v(P33-O37)(13), v(P2-O6)(12), v(P3-O10)(7)
75.	755				v(P33-O37)(19), v(P34-O41)(13), v(P2-O6)(8), v(P3-O10)(5)
76.	690	689	τ (im), δ (skel)	imidazole, skeletal vib.	τ (C48-C49-N45-C58)(17), δ (N45-C62-C60-N46)(16), δ (N45-C49-C50)(12), v(C49-N45)(9)
77.	687				τ (C17-C18-N14-C27)(15), δ (C29-C31-H32)(14), δ (N14-C18-C19)(13), τ (N14-C31-C29-N15)(11)
78.	653	650	ρ_w (H ₂ O)	H ₂ O	δ (O64-H65-O40)(49), δ (O64-H66-O36)(5)
79.	634	623	τ (im)	imidazole	τ (N45-C62-C60-N46)(57), v(C49-N45)(8), τ (C62-C60-N46-C58)(7), τ (N45-C58-N46-C60)(5)
80.	633				τ (N14-C31-C29-N15)(48), τ (C27-N15-C29-C31)(8), τ (N14-C27-N15-C29)(7)
81.	583	602	τ (im)	imidazole	τ (N45-C58-N46-C60)(39), τ (N45-C62-C60-N46)(17), τ (C62-C60-N46-C58)(8)
82.	580				τ (N14-C27-N15-C29)(44), τ (N14-C31-C29-N15)(18), τ (C31-C29-N15-C27)(9)
83.	538	560	ρ_t (H ₂ O)	H ₂ O	δ (O64-H66-O36)(36), δ (O64-H65-O40)(8)
84.	522		δ (skel), τ (skel)	skeletal vib.	δ (O43-C48-C49)(7), δ (N45-C49-C48)(6), τ (N45-C49-C48-P33)(5), δ (N45-C49-C54)(4)
85.	515				δ (P33-C48-O49)(5), δ (N45-C49-C48)(5), δ (C50-C49-C54)(4)
86.	467	486	v(Cu-O)	metal-ligand vib.	v(Cu1-O5)(6), v(Cu1-O9)(4)
87.	421	438	δ (skel)	skeletal vib.	δ (N45-C49-C50)(5), δ (N14-C18-C19)(4)
88.	419		δ (skel), δ (OPO)	skeletal vib., phosphonate O-P-O	δ (N14-C18-C19)(5), δ (O12-C17-C18)(5), δ (O8-P3-O9)(5)
89.	398	415	δ (OPO), δ (skel)	phosphonate O-P-O skeletal vib.	δ (O8-P3-O10)(9), δ (C19-C18-C23)(5), δ (O12-C17-C18)(4)
90.	396				δ (C19-C18-C23)(11), δ (O39-P34-O41)(7), δ (C17-C18-C19)(5)

^aScaling factors for the calculated harmonic frequencies: 0.943 for modes 1-27, 0.978 for modes 28-43, 1.000 for modes 44-90. ^bAbbreviations: br – broad, v – stretching, δ – in-plane bending, ρ_r – rocking, ρ_s – scissoring, ρ_w – wagging, ρ_t – twisting, γ – out-of-plane bending, τ – torsion. Subscripts: as – antisymmetric; s – symmetric. ^cVibrational bands assignment for the most characteristic functional groups based on the significant contribution in the potential energy distribution. ^dThe PED values are listed if a contributor is among the top four and is $\geq 4\%$.

Table S10. Frequencies of theoretical and experimental IR bands and their vibrational assignments of complex **3a**.

No.	Calcd ^a ν [cm ⁻¹]	Exp. ν [cm ⁻¹]	General assignment ^{b,c}	Functional group	PED ^d
1.	3639	3558	v _{as} (O–H)	H ₂ O	v(O34–H35)(43)
2.	3634		v(O–H)	phosphonate PO–H	v(O6–H7)(56)
3.	3630		v(O10–H11)(54)		
4.	3498	3448	v(N–H)	imidazole	v(N15–H16)(60)
5.	3486		v _s (O–H)	H ₂ O	v(O34–H36)(34)
6.	3283	3420-3180 br	v(O–H)	hydroxyl CO–H	v(O12–H13)(35)
7.	3172	3161	v(C–H)	imidazole	v(C32–H33)(52), v(C30–H31)(6)
8.	3145	3141			v(C28–H29)(67)
9.	3140				v(C30–H31)(43), v(C32–H33)(4)
10.	3038	3050-3000 br	v _{as} (C–H)	–CH ₂ –	v(C19–H20)(47), v(C19–H21)(11)
11.	3019				v(C25–H26)(49), v(C25–H27)(20)
12.	2991				v(C22–H23)(59), v(C22–H24)(12)
13.	2969	2981	v _s (C–H)	–CH ₂ –	v(C19–H21)(63), v(C19–H20)(15)
14.	2941	2950			v(C25–H27)(36), v(C25–H26)(15)
15.	2919	2930-2920 br			v(C22–H24)(44), v(C22–H23)(9)
16.	1627	1649 br	ρ _s (H ₂ O)	H ₂ O	δ(H35–O34–H36)(12)
17.	1563	1560 br	v(C=C), δ(im)	imidazole	δ(H16–N15–C30)(26), v(C30–C32)(15)
18.	1523		v(C=N), v(C–N)	imidazole	v(C28–N15)(21), v(C28–N14)(13)
19.	1478	1473	ρ _s (CH ₂)	–CH ₂ –	δ(H20–C19–H21)(16), δ(H23–C22–H24)(9)
20.	1443	1437	v(C–N), v(C=C), v(C=N)	imidazole	v(C30–N15)(12), v(C30–C32)(8), v(C28–N15)(7), v(C28–N14)(4)
21.	1433		ρ _s (CH ₂)	–CH ₂ –	δ(H26–C25–H27)(24), δ(C18–C25–H26)(5)
22.	1366	1354	δ(COH)	hydroxyl C–O–H	δ(C17–O12–H13)(28)
23.	1355		v(C–N)	imidazole	v(C32–N14)(13), v(C28–N14)(11)
24.	1320	1321	ρ _w (CH ₂)	–CH ₂ –	δ(C18–C25–H26)(6), δ(C18–C19–H20)(6), δ(C22–C19–H20)(6)
25.	1307		δ(im)	imidazole	δ(C28–N15–H16)(17), δ(C30–N15–H16)(16)
26.	1266	1272	ρ _w (CH ₂)	–CH ₂ –	v(C18–N14)(7), δ(C18–C25–H27)(5), δ(C22–C25–H27)(5)
27.	1262	1257			δ(H23–C22–C25)(6), δ(C19–C22–H23)(5)
28.	1243	1242	v(C–N), ρ _t (CH ₂)	imidazole, –CH ₂ –	v(C32–N14)(11), δ(C22–C25–H27)(7), v(C28–N15)(5), δ(C18–C25–H27)(5)
29.	n.o.	1224	-	-	n.o.
30.	1204	1199	v(skel)	skeletal vib.	v(C17–C18)(21)
31.	1159	1165	v(P=O), δ(POH)	phosphonate P=O	v(P2–O4)(5), δ(P2–O6–H7)(4)
32.	1143	1149			v(P2–O4)(13), δ(P2–O6–H7)(12)
33.	1089	1100	v(C–O), v(C–N)	hydroxyl C–OH, imidazole	v(C17–O12)(9), v(C30–N15)(8)

34.	1055	1063	v(P=O), δ (POH)	phosphonate P=O	v(P3–O8)(11), δ (P3–O10–H11)(7)
35.	1040	1042			δ (P2–O6–H7)(23), v(P2–O4)(16)
36.	1003	1000	$\delta_{\text{ring}}(\text{im})$, v(skel)	imidazole, skeletal vib.	δ (H16–N15–C30)(17), v(C18–N14)(4), v(C17–C18)(4)
37.	984	986	$\delta_{\text{ring}}(\text{im})$, $\delta_{\text{ring}}(\text{cbt})$	imidazole, cyclobutane	δ (H16–N15–C30)(10), v(C22–C25)(6), v(C19–C22)(6), v(C17–C18)(5)
38.	957	967	v(P=O)	phosphonate P=O	v(P3–O8)(8), v(P2–O4)(6)
39.	929	938	v(P–O)	phosphonate P–O	v(P3–O9)(17), v(P3–O8)(8)
40.	917	909			v(P2–O5)(7)
41.	886	884	$\gamma(\text{im})$	imidazole	γ (H33–C32,N14,C30)(6), δ (C17–C18–N14)(4)
42.	869				γ (H33–C32,N14,C30)(49)
43.	838	846			γ (H33–C32,N14,C30)(12), γ (H31–C30,N15,C32)(6), v(C17–P2)(4)
44.	756	770	v(P–O)	phosphonate P–OH	v(P2–O6)(14), v(P3–O10)(7)
45.	729	723			v(P3–O10)(23)
46.	656	650	$\tau(\text{im})$	imidazole	τ (C18–N14–C32–C30)(17), τ (C17–C18–N14–C28)(10)
47.	630	630			v(C18–N14)(10), τ (N14–C28–N15–C30)(5)
48.	581	596	$\rho_w(\text{H}_2\text{O})$	H ₂ O	δ (O34–H35–O40)(21)
49.	554	552	v(Cu–O)	metal-ligand vib.	v(Cu1–O5)(4)
50.	535				δ (O12–C17–C18)(4), v(Cu1–O9)(3)
51.	465	478	$\tau(\text{skel})$	skeletal vib.	τ (C25–C22–C19–C18)(5)
52.	436	420	$\delta(\text{OPO})$	phosphonate O–P–O	δ (O8–P3–O9)(10), δ (O9–P3–O10)(4)
53.	422				δ (O8–P3–O10)(7)

^aScaling factors for the calculated harmonic frequencies: 0.950 for modes 1-15, 0.975 for modes 16-23, 1.000 for modes 24-53. ^bAbbreviations: br – broad, v – stretching, δ – in-plane bending, $\delta_{\text{ring}}(\text{cbt})$ – cyclobutane ring breaching, ρ_r – rocking, ρ_s – scissoring, ρ_w – wagging, ρ_t – twisting, γ – out-of-plane bending, τ – torsion. Subscripts: as – antisymmetric; s – symmetric. ^cVibrational bands assignment for the most characteristic functional groups based on the significant contribution in the potential energy distribution. ^dThe PED values are listed if a contributor is among the top four and is $\geq 4\%$ (except vib. no. 50).

Table S11. Frequencies of theoretical and experimental IR bands and their vibrational assignments of complex **4a**.

No.	Calcd ^a ν [cm ⁻¹]	Exp. ν [cm ⁻¹]	General assignment ^{b,c}	Functional group	PED ^d
1.	3618	3564	ν(O–H), ν _{as} (O–H)	phosphonate PO–H, H ₂ O	ν(O6–H7)(38), ν(O37–H38)(8)
2.	3614				
3.	3483	3448	ν(N–H)	imidazole	ν(N15–H16)(98)
4.	3478				
5.	3274	3420-3200 br	ν(O–H)	hydroxyl CO–H	ν(O12–H13)(45)
6.	3162	3165	ν(C–H)	imidazole	ν(C35–H36)(67), ν(C33–H34)(6)
7.	3134	3142			ν(C31–H32)(68)
8.	3127				ν(C33–H34)(76), ν(C35–H36)(6)
9.	3005	3029	ν _{as} (C–H)	–CH ₂ –	ν(C19–H20)(53), ν(C19–H21)(39)
10.	2987	2950-2940 br			ν(C28–H30)(51), ν(C28–H29)(37)
11.	2962		2957	ν(C25–H27)(31), ν(C22–H23)(27), ν(C25–H26)(6)	
12.	2954	2950-2940 br	ν _s (C–H)	–CH ₂ –	ν(C19–H21)(49), ν(C19–H20)(39), ν(C25–H27)(7)
13.	2944		ν _{as} (C–H)		ν(C22–H23)(45), ν(C25–H27)(34), ν(C22–H24)(10)
14.	2929	2925	ν _s (C–H)	–CH ₂ –	ν(C28–H29)(31), ν(C28–H30)(20)
15.	2904	2910			ν(C22–H24)(36), ν(C25–H26)(15), ν(C22–H23)(10)
16.	2891	2878			ν(C25–H26)(61), ν(C22–H24)(25), ν(C25–H27)(9)
17.	1625	1645	ρ _s (H ₂ O)	H ₂ O	δ(H38–O37–H39)(15)
18.	1562	1563 br	δ(im), ν(C=C)	imidazole	δ(H16–N15–C33)(40), ν(C33–C35)(28), δ(H16–N15–C31)(24)
19.	1520		ν(C–N), ν(C=N), δ(im)		ν(C31–N15)(29), ν(C31–N14)(18), δ(H16–N15–C33)(15), δ(N15–C33–H34)(4)
20.	1490	1459	ρ _s (CH ₂)	–CH ₂ –	δ(H20–C19–H21)(17), δ(H23–C22–H24)(9), δ(H29–C28–H30)(7)
21.	1469				δ(H23–C22–H24)(17), δ(H20–C19–H21)(13), δ(H26–C25–H27)(13)
22.	1463				δ(H29–C28–H30)(22), δ(H20–C19–H21)(7)
23.	1450				δ(H26–C25–H27)(33), δ(H23–C22–H24)(17), δ(H29–C28–H30)(6), δ(H20–C19–H21)(5)
24.	1441		ν(C–N), ν(C=C), ν(C=N)	imidazole	ν(C33–N15)(13), ν(C33–C35)(10), ν(C31–N15)(9), ν(C31–N14)(5)
25.	1364	1356	ν(C–N), ρ _w (CH ₂)	imidazole, –CH ₂ –	ν(C35–N14)(14), δ(C18–C19–H20)(14), δ(H20–C19–C22)(13), ν(C31–N14)(11)
26.	1354		δ(COH)	hydroxyl C–O–H	δ(C17–O12–H13)(27)
27.	1325	1321	ρ _w (CH ₂)	–CH ₂ –	δ(C25–C28–H30)(6), δ(C18–C28–H30)(6), δ(C19–C22–H24)(5), δ(C22–C25–H26)(5)
28.	1307	1303	δ(im)	imidazole	δ(H16–N15–C33)(32), δ(H16–N15–C31)(32)
29.	1272	1239	ρ _w (CH ₂)	–CH ₂ –	δ(C18–C19–H21)(14), δ(H23–C22–C25)(11), δ(C22–C25–H26)(9), δ(C19–C22–H23)(7)
30.	1252		ν(C–N)	imidazole	ν(C18–N14)(17), ν(C35–N14)(13), ν(C31–N15)(7), δ(H23–C22–C25)(4)
31.	1223		ρ _t (CH ₂)	–CH ₂ –	δ(H27–C25–C28)(7), δ(C19–C22–H23)(5), δ(C22–C25–H27)(4), ν(C17–C18)(4)
32.	1176	1195	δ(im)	imidazole	δ(H16–N15–C31)(12), δ(H16–N15–C33)(12)

33.	1152	1161 br	v(P=O), δ (POH)	phosphonate P=O	v(P2-O4)(16), δ (P2-O6-H7)(14)
34.	1138				δ (P3-O10-H11)(30), v(P3-O8)(12)
35.	1094	1096	v(C-N)	imidazole	v(C33-N15)(18), δ (N15-C31-H32)(4), v(C18-N14)(4)
36.	1072	1063	v(C-O)	hydroxyl C-OH	v(C17-O12)(11), δ (P3-O10-H11)(5)
37.	1052		v(P=O), δ (POH)	phosphonate P=O	v(P3-O8)(18), δ (P3-O10-H11)(14)
38.	1041	1037			(P2-O6-H7)(21), v(P2-O4)(15)
39.	983	1000	$\delta_{\text{ring}}(\text{im})$	imidazole	δ (H16-N15-C33)(10)
40.	965	957	v(C-C)	-CH ₂ -CH ₂ -	v(C19-C25)(21), v(C25-C28)(20)
41.	931	934	v(P-O)	phosphonate P-O	v(P3-O9)(20), v(P3-O8)(10)
42.	916	911			v(P2-O5)(15), v(P2-O4)(7)
43.	898	887	v(C-C)	-CH ₂ -CH ₂ -	v(C22-C25)(16), v(C19-C22)(5)
44.	852	839	$\gamma(\text{im})$	imidazole	γ (H32-C31,N14,N15)(9), γ (H36-C35,N14,C33)(9), γ (H34-C33,N15,C35)(7)
45.	746	769	v(P-O)	phosphonate P-OH	v(P2-O6)(15), v(P3-O10)(6)
46.	729	739			v(P3-O10)(18)
47.	639	642	$\tau(\text{im})$	imidazole	τ (C18-N14-C35-C33)(7)
48.	626				τ (C33-C35-N14-C18)(25), τ (C35-C33-N15-C31)(13), γ (H36-C35,N14,C33)(4)
49.	578				592
50.	548	552	v(Cu-O)	metal-ligand vib.	v(Cu1-O5)(5), v(Cu1-O9)(4)
51.	460	475	$\tau(\text{skel})$	skeletal vib.	τ (C18-C19-C22-C25)(4)
52.	433	447	$\delta(\text{OPO})$	phosphonate O-P-O	δ (O8-P3-O9)(11), δ (O9-P3-O10)(4)
53.	421	412			δ (O8-P3-O10)(8)

^aScaling factors for the calculated harmonic frequencies: 0.946 for modes 1-16, 0.973 for modes 17-26, 1.000 for modes 27-53. ^bAbbreviations: br – broad, v – stretching, δ – in-plane bending, ρ_s – scissoring, ρ_w – wagging, ρ_t – twisting, γ – out-of-plane bending, τ – torsion. Subscripts: as – antisymmetric; s – symmetric. ^cVibrational bands assignment for the most characteristic functional groups based on the significant contribution in the potential energy distribution. ^dThe PED values are listed if a contributor is among the top four and is $\geq 4\%$.

Table S12. Frequencies of theoretical and experimental IR bands and their vibrational assignments of ligand **1**.

No.	Calcd ^a ν [cm ⁻¹]	Exp. ν [cm ⁻¹]	General assignment ^{b,c}	Functional group	PED ^d
1.	3685	3461 br	v(O–H)	phosphonate PO–H	v(O10–H11)(100)
2.	3536		v(N–H)	imidazole	v(N15–H16)(99)
3.	3481		v(O–H)	hydroxyl CO–H	v(O12–H13)(74)
4.	3365		v(O–H)	phosphonate PO–H	v(O5–H6)(69)
5.	3246		v(O–H)		v(O3–H4)(71)
6.	3218	3188	v(C–H)	imidazole	v(C31–H32)(71), v(C27–H28)(21), v(C29–H30)(6)
7.	3214				v(C27–H28)(77), v(C31–H32)(20)
8.	3180	3166			v(C29–H30)(92), v(C31–H32)(7)
9.	3045	3054	v _{as} (C–H)	–CH ₃	v(C19–H21)(57), v(C19–H22)(26), v(C23–H25)(4)
10.	3038				v(C23–H24)(56), v(C23–H25)(37), v(C19–H22)(4)
11.	3030				v(C19–H20)(46), v(C19–H22)(33), v(C19–H21)(14)
12.	3024				v(C23–H26)(43), v(C23–H25)(34), v(C23–H24)(15)
13.	2947	2959	v _s (C–H)	–CH ₃	v(C19–H20)(44), v(C19–H22)(22), v(C19–H21)(21), v(C23–H26)(5)
14.	2941				v(C23–H26)(47), v(C23–H25)(21), v(C23–H24)(20), v(C19–H20)(5)
15.	1573	1580	v(C=C), v(C–N), δ(im)	imidazole	δ(H16–N15–C29)(43), δ(H16–N15–C27)(32), v(C29–C31)(19), v(C27–N14)(6)
16.	1538	1535	v(C=N), v(C–N), δ(im)	imidazole	δ(C29–N15–H16)(33), v(C27–N15)(26), v(C27–N14)(15), δ(N15–C29–H30)(5)
17.	1506	1483	δ _{as} (CH ₃)	–CH ₃	δ(H24–C23–H25)(34), δ(H21–C19–H22)(20), δ(H25–C23–H26)(9), δ(H20–C19–H21)(4)
18.	1483				δ(H21–C19–H22)(32), δ(H24–C23–H25)(20), δ(H25–C23–H26)(13), δ(H20–C19–H21)(9)
19.	1446	1468	v(C=N), v(C–N), v(C=C)	imidazole	v(C29–N15)(23), v(C27–N15)(20), v(C29–C31)(18), v(C27–N14)(6)
20.	1410	1397	δ _s (CH ₃)	–CH ₃	δ(H25–C23–H26)(21), δ(C18–C23–H25)(16), δ(C18–C23–H26)(10), δ(C18–C23–H24)(9)
21.	1386	1374	δ(COH)	hydroxyl C–O–H	δ(C17–O12–H13)(79)
22.	1360	1352	v(C–N)	imidazole	v(C31–N14)(21), v(C27–N14)(17), δ(C29–C31–H32)(7), v(C29–N15)(6)
23.	1334	1323	δ(POH)	phosphonate P–O–H	δ(P1–O3–H4)(39), δ(P1–O5–H6)(26)
24.	1311	1309	δ(im)	imidazole	δ(H16–N15–C29)(34), δ(H16–N15–C27)(33), δ(N14–C31–H32)(5), δ(C29–C31–H32)(4)
25.	1263	1290-1225 br	v(skel), v(C–N), v(C=N)	skeletal vib., imidazole	v(C18–N14)(16), v(C18–C23)(12), v(C31–N14)(8), v(C27–N15)(5)
26.	1243		ρ _r (CH ₃)	–CH ₃	v(C17–C18)(24), δ(C18–C23–H26)(12), v(C18–C19)(24), δ(C18–C23–H24)(9)
27.	1224		v(skel), δ(im)	skeletal vib., imidazole	v(C18–C19)(17), v(C18–C23)(16), δ(N14–C27–H28)(8), δ(N15–C27–H28)(6)
28.	1189	1210	ρ _r (CH ₃)	–CH ₃	δ(C18–C19–H21)(12), δ(C18–C23–H25)(12), v(C18–N14)(4)
29.	1179	1179	δ(POH)	phosphonate P–O–H	δ(P1–O5–H6)(44), δ(P1–O3–H4)(33)
30.	1141	1140	v(P=O), δ(POH)	phosphonate P=O	v(P7–O8)(43), δ(P7–O10–H11)(22), v(P7–O9)(12)
31.	1098	1100	v(C–O)	hydroxyl C–OH	v(C12–O17)(49), v(C29–N15)(5)
32.	1093		v(C–N)	imidazole	v(C29–N15)(29), v(C12–O17)(13), δ(N14–C31–H32)(9), δ(C29–C31–H32)(8)

33.	1076	1079	v(P=O)	phosphonate P=O	v(P1-O2)(78)
34.	1028	1047			δ (P7-O10-H11)(67), v(P7-O8)(20), v(P7-O9)(6)
35.	1007	1005	$\delta_{\text{ring}}(\text{im})$	imidazole	δ (C29-N15-H16)(47), δ (N15-C29-H30)(5), δ (N14-C31-C29)(5), δ (N14-C27-N15)(4)
36.	977	990	$\rho_r(\text{CH}_3)$	-CH ₃	v(C17-C18)(23), δ (C18-C23-H24)(17), v(C18-C19)(15), δ (C18-C23-H26)(15)
37.	972				v(C18-C23)(21), δ (C18-C19-H22)(19), v(C17-C18)(17), δ (C18-C23-H25)(7)
38.	926	948	$\delta_{\text{ring}}(\text{im})$	imidazole	δ (C27-N15-C29)(29), δ (H16-N15-C27)(24), δ (H16-N15-C29)(14), δ (N15-C29-C31)(10)
39.	923	896 br	v(P-O)	phosphonate P-O	v(P7-O9)(41), v(P7-O8)(22)
40.	826	832	$\gamma(\text{im})$	imidazole	γ (H28-C27,N14,N15)(57), v(P1-C17)(11), v(P7-C17)(6), δ (P1-C17-C18)(5)
41.	749	747	v(P-O)	phosphonate P-OH	v(P1-O3)(29), v(P1-O5)(21)
42.	692	683			v(P7-O10)(53)
43.	633	646	$\tau(\text{im})$	imidazole	τ (N14-C27-N15-C29)(31), v(C18-N14)(10), τ (C17-C18-N14-C27)(6)
44.	629	623			τ (N14-C31-C29-N15)(58), τ (N14-C27-N15-C29)(21), τ (C31-C29-N15-C27)(13)
45.	578	547			τ (N14-C27-N15-C29)(47), τ (N14-C31-C29-N15)(16), τ (C31-C29-N15-C27)(10), τ (P1-C17-O12-H13)(5)
46.	522	500	$\delta(\text{OPO}), \delta(\text{skel})$	phosphonate O-P-O skeletal vib.	τ (H11-O10-P7-O8)(10), δ (O8-P7-O9)(8), δ (O9-P7-C17)(6), δ (O10-P7-C17)(4)
47.	468	470			δ (C19-C18-C23)(10), δ (P1-C17-O12)(8), δ (O2-P1-C17)(6), τ (H6-O5-P1-O2)(5)
48.	446	443			δ (N14-C18-C19)(15), δ (N14-C18-C23)(9), δ (C18-N14-C31)(5), δ (C18-N14-C27)(5)
49.	401	406			τ (H11-O10-P7-O8)(9), δ (O8-P7-O9)(9), δ (O9-P7-O10)(8), δ (N14-C18-C23)(6)

^aScaling factors for the calculated harmonic frequencies: 0.961 for modes 1-14, 0.976 for modes 15-22, 1.000 for modes 23-49. ^bAbbreviations: br – broad, v – stretching, δ – in-plane bending, ρ_r – rocking, γ – out-of-plane bending, τ – torsion. Subscripts: as – antisymmetric; s – symmetric. ^cVibrational bands assignment for the most characteristic functional groups based on the significant contribution in the potential energy distribution. ^dThe PED values are listed if a contributor is among the top four and is $\geq 4\%$.

Table S13. Frequencies of theoretical and experimental IR bands and their vibrational assignments of ligand **3**.

No.	Calcd ^a ν [cm ⁻¹]	Exp. ν [cm ⁻¹]	General assignment ^{b,c}	Functional group	PED ^d
1.	3651	3650-3185 br	v(O-H)	phosphonate PO-H	v(O10-H11)(100)
2.	3514		v(N-H)	imidazole	v(N15-H16)(99)
3.	3616		v(O-H)	hydroxyl CO-H	v(O12-H13)(70)
4.	3183	3175	v(C-H)	imidazole	v(C28-H29)(75), v(C32-H33)(16), v(C30-H31)(6)
5.	3178				v(C32-H33)(57), v(C28-H29)(23), v(C30-H31)(17)
6.	3157	3150			v(C30-H31)(75), v(C32-H33)(24)
7.	3046	3058	v _{as} (C-H)	-CH ₂ -	v(C25-H26)(49), v(C22-H24)(19), v(C25-H27)(9), v(C22-H23)(7)
8.	3047		v(O-H)	phosphonate PO-H	v(O5-H6)(65), v(O3-H4)(6)
9.	3040		v _{as} (C-H)	-CH ₂ -	v(C19-H21)(53), v(C25-H26)(24), v(C19-H20)(11), v(C22-H24)(4)
10.	3028				v(C22-H24)(46), v(C19-H21)(22), v(C22-H23)(16), v(C25-H26)(12)
11.	2969	2971	v _s (C-H)	-CH ₂ -	v(C22-H23)(66), v(C22-H24)(27)
12.	2963		v(O-H)	phosphonate PO-H	v(O3-H4)(71), v(O5-H6)(6)
13.	2953		v _s (C-H)	-CH ₂ -	v(C25-H27)(46), v(C19-H20)(32), v(C25-H26)(7), v(C19-H21)(5)
14.	2951				v(C19-H20)(49), v(C25-H27)(34), v(C19-H21)(9), v(C25-H26)(5)
15.	1572	1577	v(C=C), v(C-N), δ(im)	imidazole	δ(H16-N15-C30)(33), δ(H16-N15-C28)(24), v(C30-C32)(17), v(C28-N14)(5)
16.	1537	1535	v(C=N), v(C-N), δ(im)	imidazole	δ(H16-N15-C30)(28), v(C28-N15)(23), v(C28-N14)(14), δ(N15-C30-H31)(5)
17.	1477	1473	ρ _s (CH ₂)	-CH ₂ -	δ(H23-C22-H24)(22), δ(H20-C19-H21)(16), δ(H26-C25-H27)(12)
18.	1450	1436			δ(H20-C19-H21)(32), δ(H26-C25-H27)(18), δ(C18-C19-H21)(5), δ(C18-C19-H20)(5)
19.	1444	1426	v(C=N), v(C-N), v(C=C)	imidazole	v(C30-N15)(23), v(C28-N15)(22), v(C30-C32)(18), v(C28-N14)(6)
20.	1373	1366	δ(COH), δ(POH)	hydroxyl C-O-H, phosphonate P-O-H	δ(C17-O12-H13)(28), δ(P1-O3-H4)(20), δ(P1-O5-H6)(16)
21.	1356	1350	v(C-N)	imidazole	v(C32-N14)(22), v(C28-N14)(19), δ(H16-N15-C28)(7), v(C30-N15)(7)
22.	1350		δ(COH), δ(POH)	hydroxyl C-O-H, phosphonate P-O-H	δ(C17-O12-H13)(42), δ(P1-O3-H4)(26), v(C17-C18)(8)
23.	1316	1312	δ(im)	imidazole	δ(H16-N15-C30)(52), δ(C30-C32-H33)(7), δ(N14-C28-H29)(7), δ(H31-C30-C32)(5)
24.	1308		ρ _w (CH ₂)	-CH ₂ -	δ(C22-C25-H26)(18), δ(C18-C25-H26)(16), δ(C22-C25-H27)(9), δ(C18-C19-H21)(6)
25.	1288	ρ _t (CH ₂)	δ(C18-C25-H27)(12), δ(C22-C25-H27)(10), δ(C18-C19-H20)(7), v(C18-N14)(7)		
26.	1280	ρ _w (CH ₂)	δ(H24-C22-C25)(18), δ(C19-C22-H24)(18), δ(H23-C22-C25)(10), δ(C19-C22-H23)(10)		
27.	1263	1261	v(C-N)	imidazole	v(C18-N14)(15), v(C32-N14)(13), δ(H20-C19-C22)(6), v(C28-N15)(5)
28.	1227	1235	ρ _t (CH ₂)	-CH ₂ -	δ(H23-C22-C25)(12), δ(H21-C19-C22)(11), δ(C19-C22-H23)(10), δ(C22-C25-H26)(8)
29.	1187	1191	v(skel)	skeletal vib.	v(C17-C18)(26), δ(H21-C19-C22)(10), v(C17-O12)(5), δ(C22-C25-H26)(5)
30.	1119	1129	v(P=O), δ(POH)	phosphonate P=O	δ(P7-O10-H11)(49), v(P7-O8)(14), v(P7-O9)(8)
31.	1087	1097	v(C-O), v(C-N)	hydroxyl C-OH, imidazole	v(C12-O17)(26), v(C30-N15)(16), δ(C18-C19-H20)(5), δ(C18-C19-H21)(4)

32.	1080	1057	$\nu(\text{P}=\text{O})$	phosphonate P=O	$\nu(\text{P1-O2})(69)$
33.	1037	1020	$\nu(\text{P}=\text{O}), \delta(\text{POH})$	phosphonate P=O	$\delta(\text{P7-O10-H11})(36), \nu(\text{P7-O8})(22), \nu(\text{P7-O9})(15)$
34.	997	987	$\delta_{\text{ring}}(\text{im})$	imidazole	$\delta(\text{H16-N15-C30})(38), \delta(\text{N14-C32-C30})(5), \nu(\text{C18-N14})(5), \delta(\text{N15-C30-H31})(5)$
35.	975	952	$\nu(\text{C}-\text{C})$	-CH ₂ -CH ₂ -	$\nu(\text{C22-C25})(39), \nu(\text{C17-C18})(12)$
36.	967				$\nu(\text{C19-C22})(39), \nu(\text{C17-C18})(10)$
37.	942	934	$\delta(\text{skel})$	skeletal vib.	$\nu(\text{C17-C18})(9), \delta(\text{N14-C18-C17})(6), \delta(\text{P1-C17-C18})(6), \delta(\text{H16-N15-C30})(6)$
38.	917	910	$\nu(\text{P}-\text{O})$	phosphonate P-O	$\nu(\text{P7-O9})(27), \nu(\text{P7-O8})(23), \nu(\text{P7-O10})(12)$
39.	858	869	$\nu(\text{P}-\text{O})$	phosphonate P-OH	$\nu(\text{P1-O5})(19), \nu(\text{P1-O3})(12), \gamma(\text{H29-C28,N14,N15})(8), \delta(\text{N14-C18-C17})(4)$
40.	848	851	$\gamma(\text{im})$	imidazole	$\gamma(\text{H33-C32,N14,C30})(51), \gamma(\text{H31-C30,N15,C32})(26), \tau(\text{N14-C32-C30-N15})(9)$
41.	834	832			$\gamma(\text{H29-C28,N14,N15})(59), \tau(\text{N14-C28-N15-C30})(5)$
42.	759	757	$\nu(\text{P}-\text{O})$	phosphonate P-OH	$\nu(\text{P1-O3})(22), \nu(\text{P7-O10})(22), \nu(\text{P1-O5})(18)$
43.	722	725			$\nu(\text{P7-O10})(32), \gamma(\text{H31-C30,N15,C32})(30), \gamma(\text{H33-C32,N14,C30})(14)$
44.	682	677	$\tau(\text{im})$	imidazole	$\tau(\text{C17-C18-N14-C28})(25), \tau(\text{N14-C32-C30-N15})(16), \tau(\text{N14-C28-N15-C30})(10)$
45.	630	637			$\tau(\text{N14-C28-N15-C30})(38), \tau(\text{P1-C17-O12-H13})(21), \tau(\text{C17-C18-N14-C28})(7)$
46.	612	623	$\tau(\text{skel})$	skeletal vib.	$\tau(\text{P1-C17-O12-H13})(64), \tau(\text{N14-C32-C30-N15})(5)$
47.	577	566	$\tau(\text{im})$	imidazole	$\tau(\text{N14-C28-N15-C30})(55), \tau(\text{N14-C32-C30-N15})(20), \tau(\text{C32-C30-N15-C28})(12)$
48.	544	552	$\delta(\text{skel})$	skeletal vib.	$\delta(\text{C17-C18-C25})(13), \delta(\text{P1-C17-C18})(8), \tau(\text{N14-C18-C17-P1})(8), \delta(\text{P7-C17-C18})(7)$
49.	516	511			$\tau(\text{N14-C18-C17-P1})(6), \delta(\text{O12-C17-C18})(5), \delta(\text{O10-P7-C17})(4), \delta(\text{O8-P7-C17})(4)$
50.	476	478	$\delta(\text{OPO}), \delta(\text{skel})$	phosphonate O-P-O skeletal vib.	$\delta(\text{O9-P7-O10})(8), \nu(\text{C17-P1})(7), \delta(\text{O2-P1-C17})(5), \delta(\text{O8-P7-C17})(5)$
51.	444	437			$\delta(\text{O2-P1-O5})(6), \delta(\text{O10-P7-C17})(4), \delta(\text{O3-P1-C17})(4)$

^aScaling factors for the calculated harmonic frequencies: 0.955 for modes 1-14, 0.975 for modes 15-22, 1.000 for modes 23-51. ^bAbbreviations: br – broad, ν – stretching, δ – in-plane bending, ρ_s – scissoring, ρ_w – wagging, ρ_t – twisting, γ – out-of-plane bending, τ – torsion. Subscripts: as – antisymmetric; s – symmetric. ^cVibrational bands assignment for the most characteristic functional groups based on the significant contribution in the potential energy distribution. ^dThe PED values are listed if a contributor is among the top four and is $\geq 4\%$.

Table S14. Frequencies of theoretical and experimental IR bands and their vibrational assignments of of ligand **4**.

No.	Calcd ^a ν [cm ⁻¹]	Exp. ν [cm ⁻¹]	General assignment ^{b,c}	Functional group	PED ^d
1.	3641	3650-3225 br	v(O–H)	phosphonate PO–H	v(O8–H9)(99)
2.	3629				v(O10–H11)(80)
3.	3604		v(N–H)	imidazole	v(O4–H5)(76)
4.	3507				v(N15–H16)(99)
5.	3200	3197	v(C–H)	imidazole	v(C35–H36)(93), v(C33–H34)(4)
6.	3175	3178			v(C31–H32)(97)
7.	3156	3155			v(C33–H34)(90), v(C35–H36)(4), δ(C33–C35–H36)(4)
8.	3011	3014	v _{as} (C–H)	–CH ₂ –	v(C28–H29)(63), v(C28–H30)(27)
9.	3003	3008			v(C19–H21)(50), v(C19–H20)(37), v(C28–H29)(5)
10.	2986	2975	v(C25–H27)(36), v(C22–H23)(30), v(C25–H26)(12), v(C22–H24)(7)		
11.	2968	2962	v _{as} /v _s (C–H)		v(C22–H23)(43), v(C25–H27)(23), v(C28–H30)(9), v(C28–H29)(8)
12.	2951	2941	v _s (C–H)		v(C19–H20)(48), v(C19–H21)(43)
13.	2933	2918			v(C25–H26)(54), v(C25–H27)(22), v(C22–H24)(15), v(C22–H23)(4)
14.	2919	2908		v(C22–H24)(64), v(C25–H26)(18), v(C22–H23)(13), v(C25–H27)(3)	
15.	2564	n.o.	v(O–H)	hydroxyl CO–H	v(O12–H13)(89)
16.	1581	1578	δ(im), v(C=C)	imidazole	δ(N14–C35–H36)(36), v(C33–C35)(13), δ(H16–N15–C33)(13), δ(H16–N15–C31)(8)
17.	1544	1534	δ(COH)	hydroxyl C–O–H	δ(C17–O12–H13)(90)
18.	1540		v(C–N), v(C=N), δ(im)	imidazole	v(C31–N15)(42), δ(H16–N15–C33)(16), v(C31–N14)(15), δ(N15–C33–H34)(13)
19.	1507	1509	ρ _s (CH ₂)	–CH ₂ –	δ(H29–C28–H30)(21), δ(H20–C19–H21)(20), δ(H26–C25–H27)(13), δ(H23–C22–H24)(7)
20.	1488	1478			δ(H20–C19–H21)(31), δ(H26–C25–H27)(27), δ(H23–C22–H24)(5), δ(C18–C19–H21)(5)
21.	1486				δ(H29–C28–H30)(43), δ(H23–C22–H24)(20), δ(H20–C19–H21)(8)
22.	1447	1460	v(C–N), v(C=C), v(C=N)	imidazole	v(C33–N15)(31), v(C31–N15)(26), v(C33–C35)(23), v(C31–N14)(5)
23.	1376	1356	v(C–N)		v(C35–N14)(27), v(C31–N14)(13), δ(H34–C33–C35)(11), δ(C33–C35–H36)(8)
24.	1355		ρ _w (CH ₂)	–CH ₂ –	δ(H21–C19–C22)(14), δ(C18–C19–H21)(12), δ(C25–C28–H30)(9), δ(C18–C28–H30)(8)
25.	1317				1317
26.	1270	1283	ρ _w /ρ _t (CH ₂)	–CH ₂ –	δ(C18–C28–H29)(10), δ(C33–C35–H36)(9), v(C18–N14)(7), δ(H24–C22–C25)(5)
27.	1254	1246	ρ _t (CH ₂)		δ(C22–C25–H27)(10), δ(H23–C22–C25)(9), v(C35–N14)(8), δ(C22–C25–H26)(8)
28.	1225	1220			δ(C19–C22–H23)(11), v(C17–C18)(10), δ(H27–C25–C28)(8), δ(C19–C22–H24)(6)
29.	1172	1199	δ(im)	imidazole	δ(H16–N15–C31)(26), δ(N15–C31–H32)(11), δ(N14–C31–H32)(9)
30.	1139	1146	v(P=O), δ(POH)	phosphonate P=O	v(P6–O7)(31), δ(P6–O8–H9)(19), v(C17–C18)(15), δ(P6–O10–H11)(12)
31.	1129	1111	δ(im)	imidazole	δ(C33–C35–H36)(38), δ(N14–C35–H36)(32), δ(H34–C33–C35)(10), δ(N15–C33–H34)(9)
32.	1090	1094	v(C–N)		v(C33–N15)(51), δ(C31–N14–C35)(15), v(C18–N14)(8)

33.	1075	1063	$\nu(\text{P}=\text{O}), \delta(\text{POH})$	phosphonate P=O	$\nu(\text{P1-O3})(32), \nu(\text{P1-O2})(15), \delta(\text{P1-O4-H5})(14), \nu(\text{C17-O12})(12)$
34.	1065		$\nu(\text{C-O})$	hydroxyl C-OH	$\nu(\text{C17-O12})(19), \nu(\text{C22-C25})(13), \nu(\text{C25-C28})(9), \nu(\text{P1-O3})(7)$
35.	1048	1042	$\nu(\text{P}=\text{O}), \delta(\text{POH})$	phosphonate P=O	$\nu(\text{P6-O7})(17), \delta(\text{P1-O4-H5})(12), \delta(\text{P6-O8-H9})(9), \nu(\text{P1-O3})(9)$
36.	1041		$\nu(\text{C-O})$	hydroxyl C-OH	$\nu(\text{C17-O12})(24), \delta(\text{C33-C35-H36})(12), \nu(\text{C19-C22})(9), \nu(\text{C22-C25})(9)$
37.	1021	1019	$\delta_{\text{ring}}(\text{im})$	imidazole	$\delta(\text{H16-N15-C33})(14), \delta(\text{H34-C33-N15})(11), \nu(\text{C18-N14})(7), \delta(\text{C31-N14-C35})(7)$
38.	979				$\delta(\text{N14-C35-C33})(36), \delta(\text{C31-N14-C35})(8), \delta(\text{H16-N15-C33})(6), \delta(\text{N14-C31-N15})(4)$
39.	966	960	$\nu(\text{C-C})$	-CH ₂ -CH ₂ -	$\nu(\text{C25-C28})(24), \nu(\text{C19-C22})(5), \nu(\text{C18-C28})(4)$
40.	942	937	$\delta(\text{skel}), \nu(\text{skel})$	skeletal vib.	$\delta(\text{N14-C18-C17})(7), \nu(\text{C18-C19})(7), \delta(\text{P1-C17-C18})(6), \nu(\text{P6-C17})(6)$
41.	910	901 br	$\nu(\text{P-O})$	phosphonate P-O	$\nu(\text{P1-O2})(55), \nu(\text{P1-O3})(13), \nu(\text{P1-O4})(12)$
42.	843	834	$\gamma(\text{im})$	imidazole	$\gamma(\text{H34-C33,N15,C35})(47), \tau(\text{N14-C35-C33-N15})(18)$
43.	822				$\gamma(\text{H32-C31,N14,N15})(61), \tau(\text{N14-C31-N15-C33})(13)$
44.	740	758 br	$\nu(\text{P-O})$	phosphonate P-OH	$\nu(\text{P1-O4})(40), \nu(\text{P1-O2})(8), \delta(\text{O12-C17-C18})(5)$
45.	724				$\nu(\text{P6-O10})(33), \nu(\text{P6-O8})(19), \nu(\text{P1-O4})(8)$
46.	645	643	$\tau(\text{im}), \delta_{\text{ring}}(\text{cpt})$	imidazole, cyclopent	$\tau(\text{N14-C31-N15-C33})(20), \delta(\text{C22-C25-C28})(9), \delta(\text{C19-C22-C25})(9), \delta(\text{C19-C22-H24})(5)$
47.	632	624	$\tau(\text{im})$	imidazole	$\tau(\text{N14-C35-C33-N15})(63), \tau(\text{C35-C33-N15-C31})(8), \tau(\text{N14-C31-N15-C33})(5)$
48.	582	588			$\tau(\text{N14-C31-N15-C33})(49), \tau(\text{N14-C35-C33-N15})(21), \tau(\text{C35-C33-N15-C31})(10)$
49.	492	483	$\delta(\text{OPO})$	phosphonate O-P-O	$\delta(\text{O7-P6-O10})(11), \delta(\text{O8-P6-O10})(11), \delta(\text{O10-P6-C17})(6), \nu(\text{P6-C17})(5)$
50.	436	454			$\delta(\text{O2-P1-O3})(22), \delta(\text{O7-P6-O10})(9), \delta(\text{O8-P6-O10})(6), \delta(\text{O10-P6-C17})(4)$
51.	412	429			$\delta(\text{O3-P1-O4})(14), \delta(\text{O12-C17-C18})(8), \delta(\text{O7-P6-O10})(5), \delta(\text{O7-P6-O8})(4)$

^aScaling factors for the calculated harmonic frequencies: 0.953 for modes 1-15, 0.984 for modes 16-25, 1.000 for modes 26-51. ^bAbbreviations: br – broad, ν – stretching, δ – in-plane bending, ρ_s – scissoring, ρ_w – wagging, ρ_t – twisting, γ – out-of-plane bending, τ – torsion. Subscripts: as – antisymmetric; s – symmetric. ^cVibrational bands assignment for the most characteristic functional groups based on the significant contribution in the potential energy distribution. ^dThe PED values are listed if a contributor is among the top four and is $\geq 4\%$.

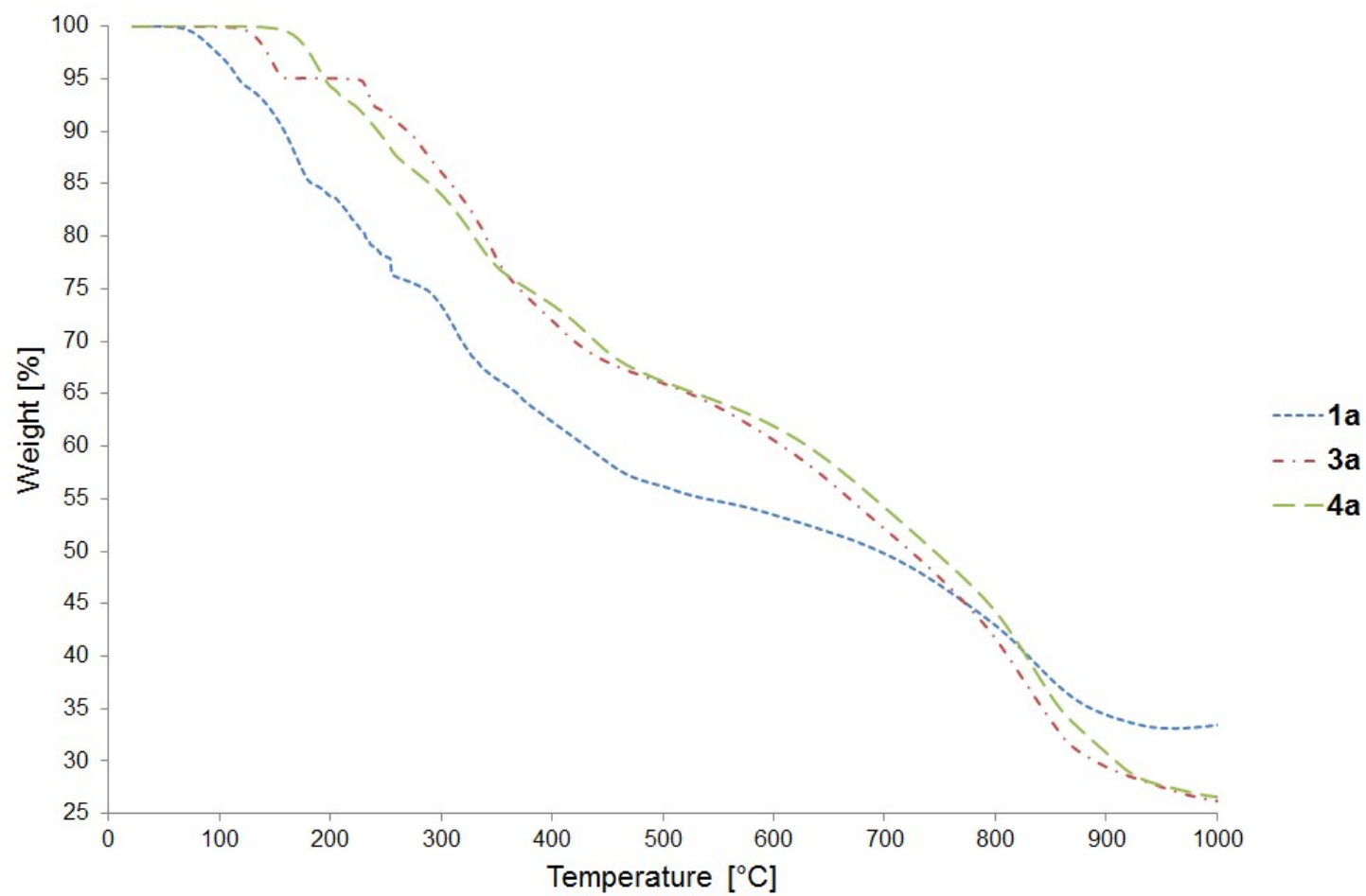


Figure S21. TG curves recorded for **1a**, **3a** and **4a**.

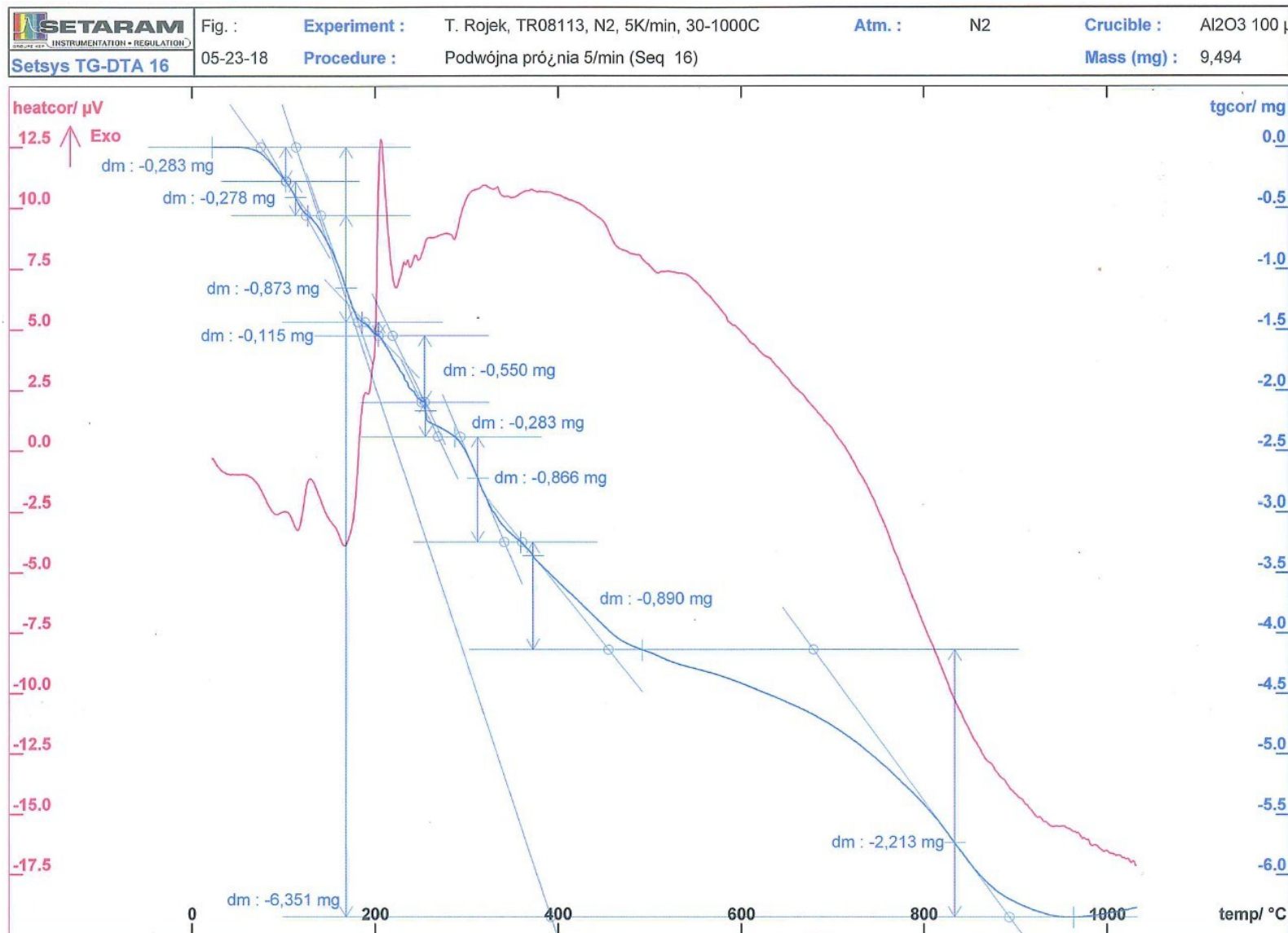


Figure S22. TG-DTA plot for the complex **1a**.

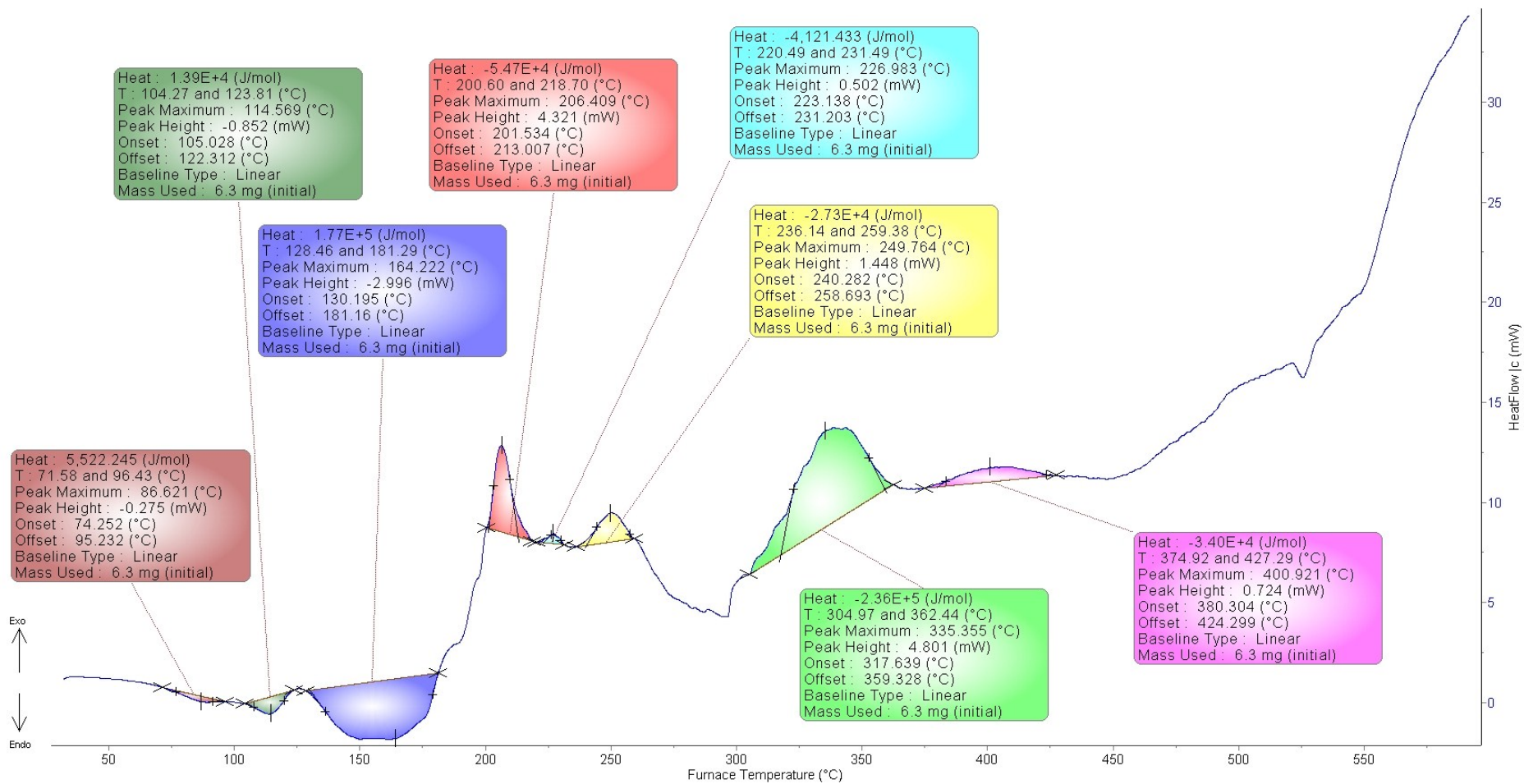


Figure S23. DSC plot for the complex 1a.

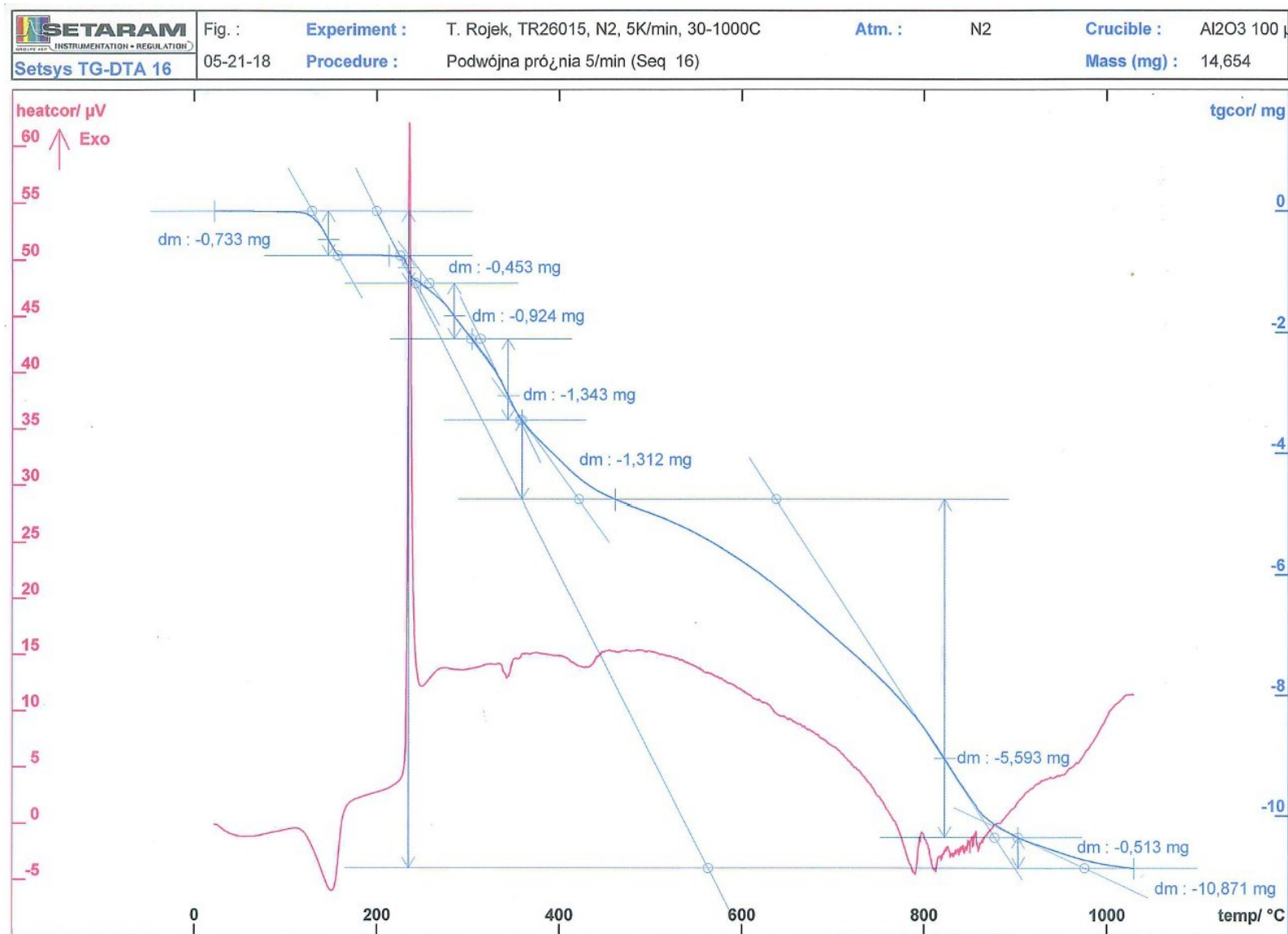


Figure S24. TG-DTA plot for the complex **3a**.

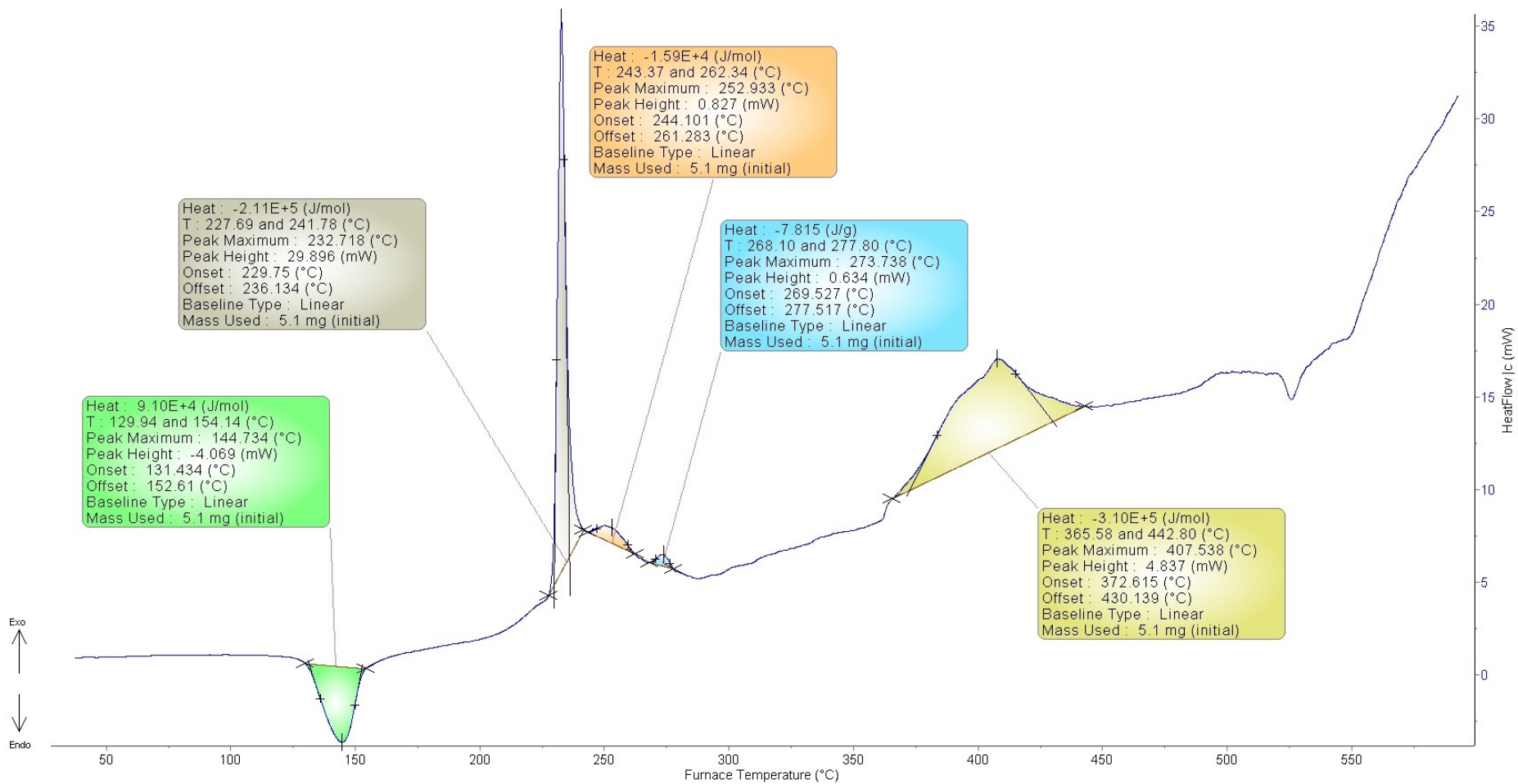


Figure S25. DSC plot for the complex 3a.

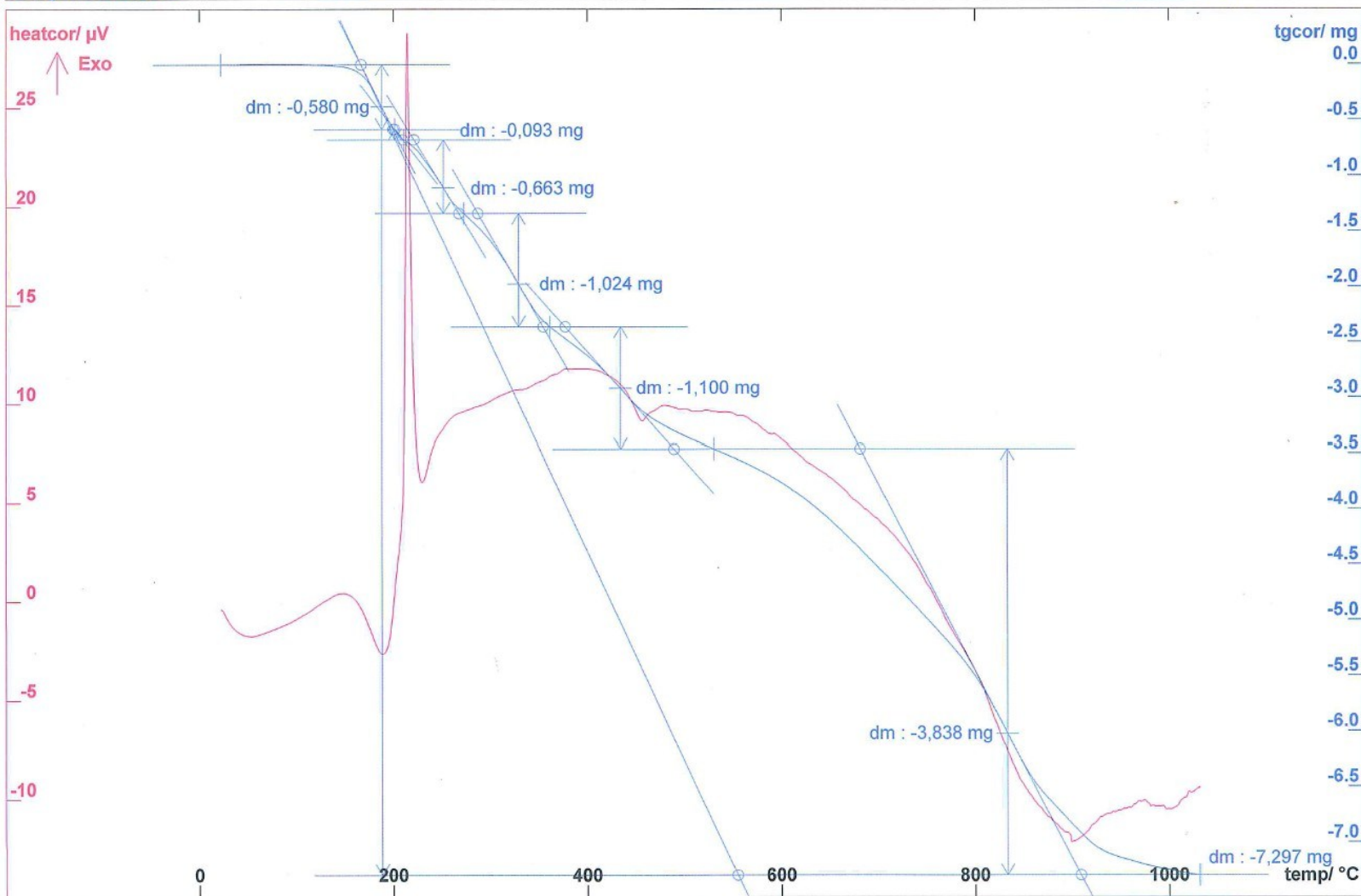


Figure S26. TG-DTA plot for the complex 4a.

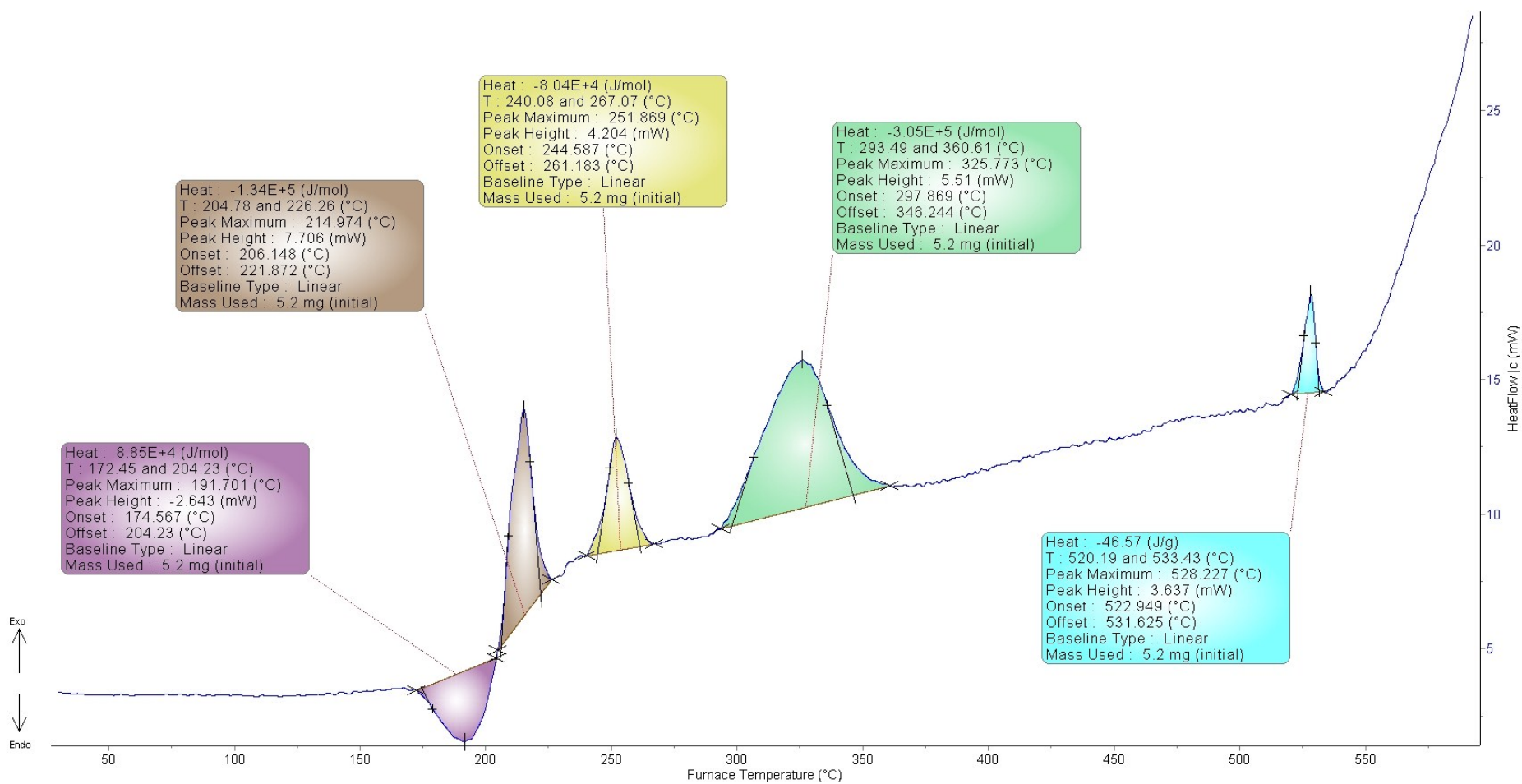


Figure S27. DSC plot for the complex 4a.

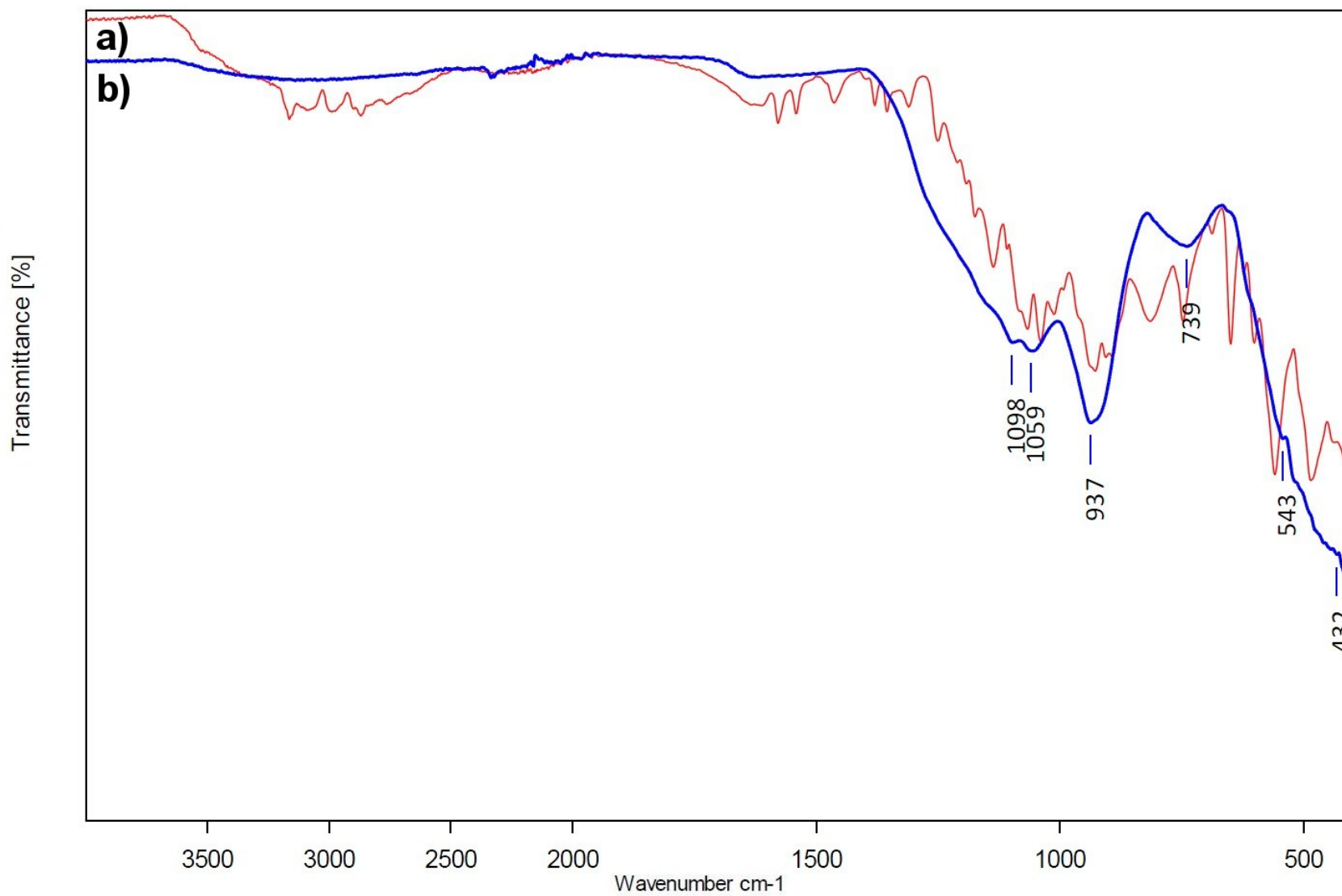


Figure S28. IR spectra of (a) crystalline complex **1a** and (b) solid obtained by heating sample of the complex up to 600 °C.

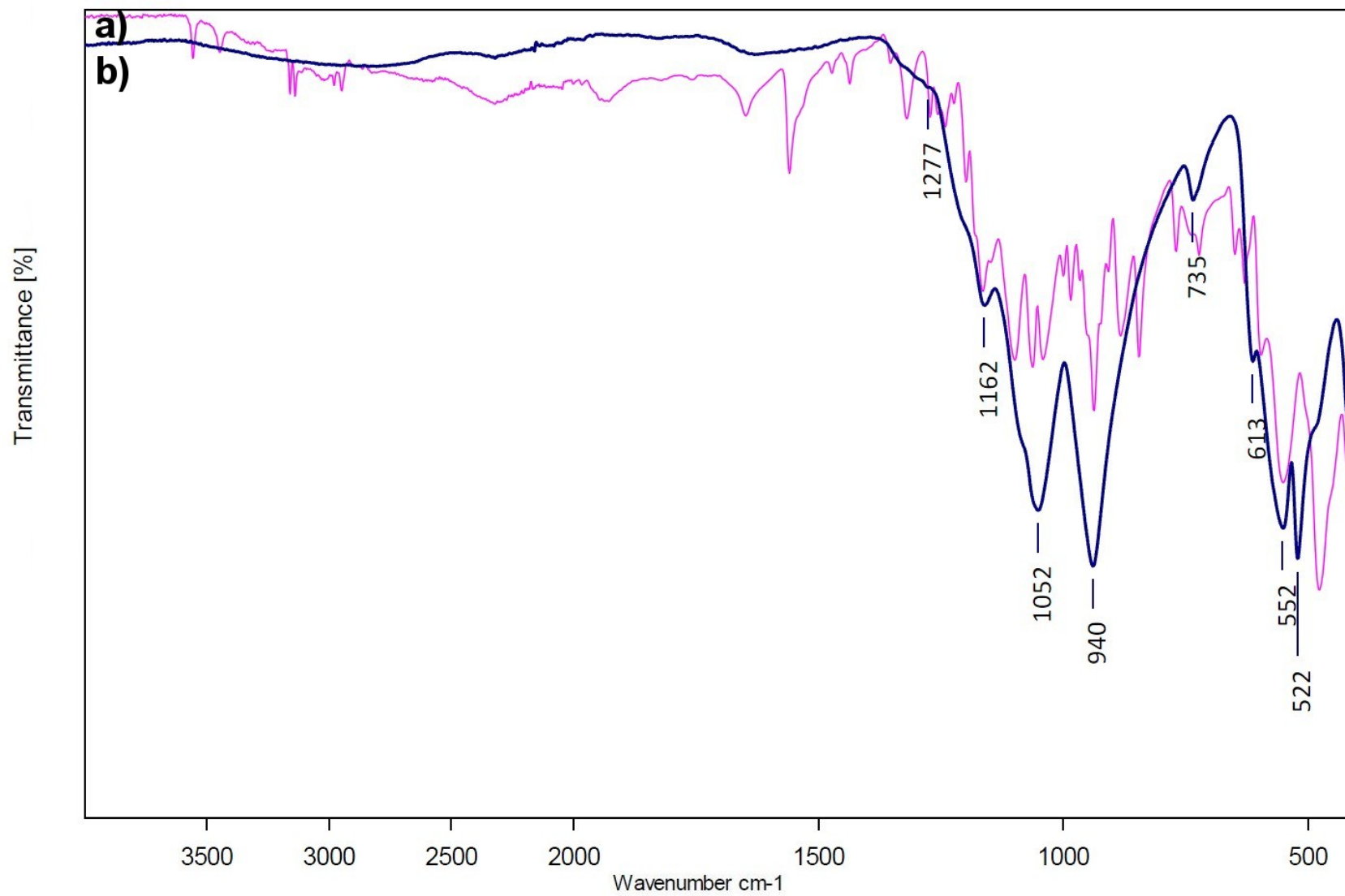


Figure S29. IR spectra of (a) crystalline complex **3a** and (b) solid obtained by heating sample of the complex up to 600 °C.

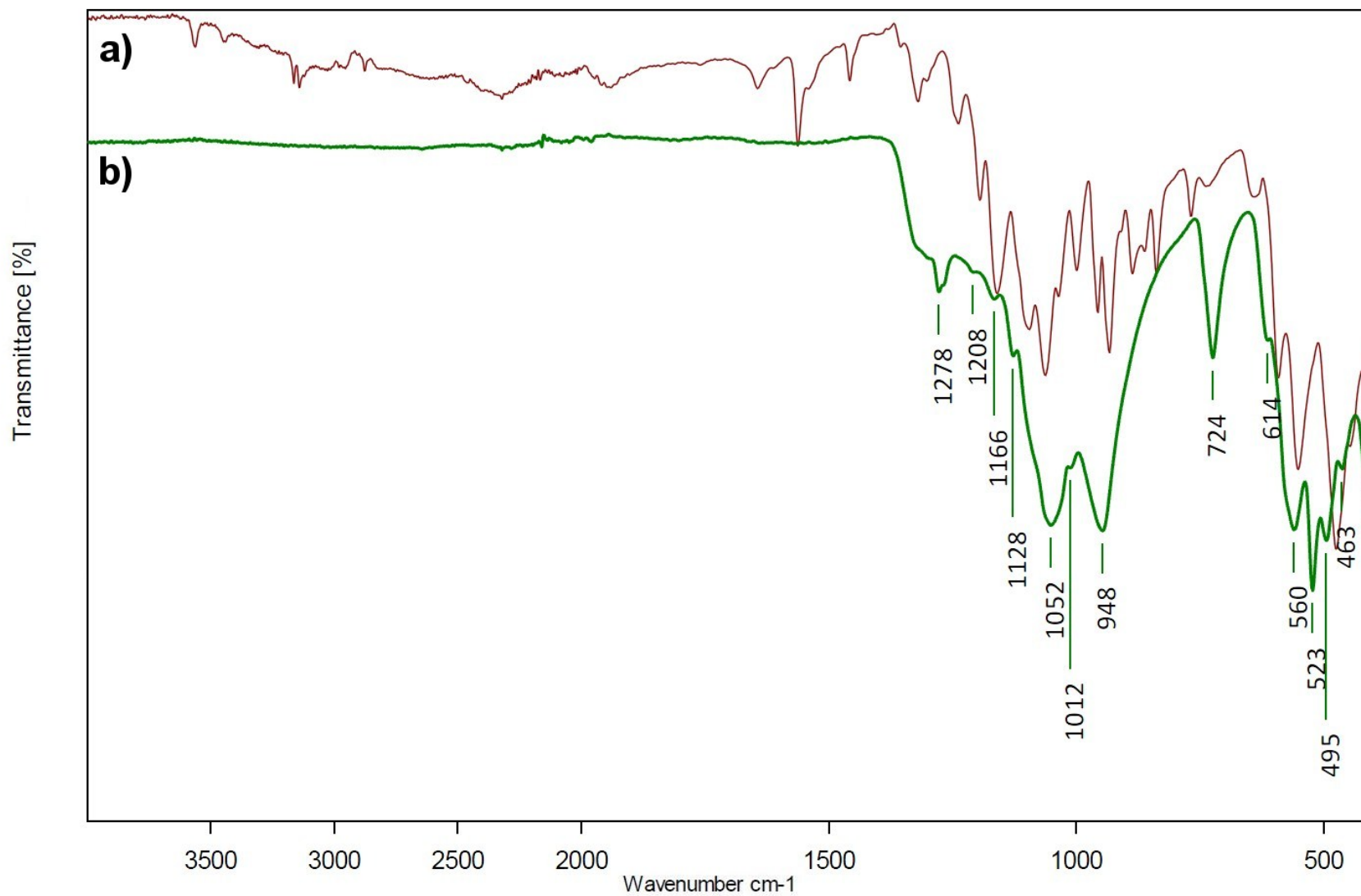


Figure S30. IR spectra of (a) crystalline complex **4a** and (b) solid obtained by heating sample of the complex up to 600 $^{\circ}\text{C}$.