## **Electronic Supplementary Information**

# Cyclam derivatives containing three acetate pendant arms: synthesis, acid-base, metal complexation and structural studies

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<b>Fig. S4</b> Species distribution diagram for $Cu^{2+}$ -H <sub>3</sub> te3a at $C_M = C_L = 1 \times 10^{-3} \text{ mol dm}^{-3}$ 7	'
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### References

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$\begin{array}{llllllllllllllllllllllllllllllllllll$		$\Pi \cdots A / A^*$	$D \cdot \cdot \cdot A / A^{\circ}$	$D-\Pi \cdots A/s^{2}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	(Hte3am)I.MeOH 1			
N(11)-H(11B)-···N(4) 2.55(2) 3.222(2) 133(2)   N(23)-H(23A)···N(8) 2.49(2) 2.829(2) 103(2)   N(17)H(17A)···O(101) [x-1/2, -y+5/2, z-1/2] 2.03(2) 2.883(2) 167(2)   N(11)-H(11A)···O(161) 2.05(2) 2.962(2) 141(2)   N(17)-H(17B)···O(161) [-x, -y+3, -z] 2.08(2) 2.951(2) 177(2)   N(11)-H(11B)···O(161) 2.06(2) 2.874(2) 148(2)   N(23)-H(23A)···O(191) 2.11(2) 2.931(2) 152(2)   N(20)-H(20B)···I [-x+1, -y+1, -z] 2.84(2) 3.696(2) 169(2)   N(20)-H(23B)···I [-x+1, -y+1, -z] 2.97(2) 3.792(1) 160(2)   O(101)-H(10F)···I 2.71(3) 3.537(1) 173(2)   (H <sub>2</sub> te2lac)CII-0.25H <sub>2</sub> O 2 2.15 2.815(9) 129   N(24)-H(24)···O(160) [-x+1/2, -y+1/2, -z] 2.15 2.815(9) 129   N(24)-H(24)···O(161) [-x+1, -y+1, -z+2] <sup>c</sup> 1.92 2.81(1) 165   (H <sub>4</sub> te2a2p <sup>OE2</sup> )(I <sub>5</sub> ) <sub>2</sub> ·0.5I <sub>2</sub> 3 3.035(7) 170   N(4)-H(4)···O(161) [-x+1, -y+1, -z+2] <sup>c</sup> 1.92 2.81(1) 165   (H <sub>4</sub> te3a1p)(CIO <sub>4</sub> ) <sub>2</sub> .4.	N(11)–H(11A)···N(1)	2.25(2)	2.890(2)	133(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N(11)-H(11B)\cdots N(4)$	2.55(2)	3.222(2)	133(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(23)–H(23A)····N(8)	2.49(2)	2.829(2)	103(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N(17)H(17A)\cdots O(101) [x-1/2, -y+5/2, z-1/2]$	2.03(2)	2.883(2)	167(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(11)–H(11A)···O(161)	2.26(2)	2.962(2)	141(2)
N(11)-H(11B)-··O(191)2.08(2)2.874(2)148(2)N(23)-H(23A)···O(191)2.11(2)2.931(2)152(2)N(20)-H(20B)···I [-x+1, -y+1, -z]2.84(2)3.696(2)169(2)N(12)-H(10F)···I2.71(3)3.537(1)173(2)(H2te2lac)ClI·0.25H2O <b>2</b> N(14)-H(14)···Cl [x-1/2, -y+1/2, z]2.152.815(9)129N(24)-H(24)···O(100) [-x-1/2, y-1/2, -z]2.152.815(9)129N(24)-H(24)···O(160) [-x-1/2, y-1/2, -z]2.583.292(7)136(H4te2a2p <sup>OEt2</sup> )(I_3) <sub>2</sub> ·0.5I <sub>2</sub> <b>31</b> 169N(24)-H(24)···O(161) [-x+2, -y+2, -z+1] <sup>b</sup> 1.882.77(1)169N(24)-H(24)···O(361) [-x+1, -y+1, -z+2] <sup>c</sup> 1.922.81(1)165(H7te3a1p)(ClO4) <sub>2</sub> .4.25H2O <b>411</b> N(4)-H(4)···O(182)2.192.720(4)115N(8)-H(8)···O(202)2.392.718(5)101N(11)-H(11)···O(222)2.322.703(4)148N(11)-H(11)···O(182) [-x-1/2, y, z]2.453.039(4)121N(8)-H(8)···O(700) [-x+1/2, y, z-1/2]1.932.820(5)159[Cu2(Hte3a)(H2O)3CI]Clo <sub>3</sub> ClO4 <sub>30</sub> -2H2O <b>5</b> <sup>d</sup> <b>01</b> N(1)-H(1)···O(182) [-x+1/2, y+1/2, z+1/2]1.86(5)2.677(7)170(6)O(1)-H(B)···O(181) [x+1/2, -y+1/2, z+1/2]1.90(4)2.726(8)178(7)O(2)-H(C)···O(182) [-x+1/2, -y+1/2, z+1/2]1.90(6)3.246(4)159(6)O(2)-H(D)···C(1) [-x+1, -y, -z+2]2.46(6)3.246(4)159(6)O(2)-H(E)···O(	$N(17)-H(17B)\cdots O(161)[-x, -y+3, -z]$	2.08(2)	2.951(2)	177(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N(11)-H(11B)\cdotsO(191)$	2.08(2)	2.874(2)	148(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N(23)-H(23A)\cdots O(191)$	2.11(2)	2.931(2)	152(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N(20)-H(20B)\cdots I[-x+1, -y+1, -z]$	2.84(2)	3.696(2)	169(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N(23) - H(23B) \cdots I$	2.97(2)	3.792(1)	160(2)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O(101)–H(10F)…I	2.71(3)	3.537(1)	173(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$(H_2 te 2 lac) ClI \cdot 0.25 H_2 O 2$			
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(14)–H(14)····Cl [ $x$ -1/2, - $v$ +1/2, $z$ ]	2.13	3.035(7)	170
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N(24)-H(24)\cdots O(100) [-x-1/2, y-1/2, -z]$	2.15	2.815(9)	129
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	N(24)–H(24)····Cl [ $x$ -1/2, - $y$ +1/2, $z$ ]	2.58	3.292(7)	136
N(4)-H(4)···O(161) $[-x+2, -y+2, -z+1]^b$ 1.882.77(1)169N(24)-H(24)···O(361) $[-x+1, -y+1, -z+2]^c$ 1.922.81(1)165(H7te3a1p)(ClO4)2.4.25H2O $d^d$ 2.192.720(4)115N(4)-H(4)···O(182)2.392.718(5)101N(1)-H(1)···O(202)2.322.720(5)106N(4)-H(4)···O(163) $[x-1/2, -y+1, z]$ 1.872.703(4)148N(11)-H(11)···O(201) $[x+1/2, -y, z]$ 2.273.080(5)145N(11)-H(11)···O(182) $[-x-1/2, y, z-1/2]$ 2.453.039(4)121N(8)-H(8)···O(700) $[-x+1/2, y, z-1/2]$ 1.932.820(5)159[Cu2(Hte3a)(H2O)_3Cl]Cl_{0.5}(ClO4)_{0.5}·2H2O $5^d$ 00O(1)-H(B)···O(181) $[x+1/2, -y+1/2, z+1/2]$ 1.86(5)2.677(7)170(6)O(2)-H(C)···O(182) $[x+1/2, -y+1/2, z+1/2]$ 1.90(4)2.726(8)178(7)O(2)-H(D)···Cl(1)[-x+1, -y, -z+2]2.46(6)3.246(4)159(6)O(2)-H(F)···O(202) $[-x+1/2, y-1/2, -z+3/2]$ 1.93(6)2.720(8)159(6)	$(H_4 te 2a 2p^{OEt2})(I_3)_2 \cdot 0.5 I_2$ 3			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$N(4) - H(4) \cdots O(161) [-x+2, -y+2, -7+1]^{b}$	1.88	2.77(1)	169
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$N(24)-H(24)\cdots O(361) [-x+1, -v+1, -z+2]^{c}$	1.92	2.81(1)	165
N(4)-H(4)O(182) $2.19$ $2.720(4)$ $115$ N(8)-H(8)O(202) $2.39$ $2.718(5)$ $101$ N(11)-H(11)O(222) $2.32$ $2.720(5)$ $106$ N(4)-H(4)O(163) [ $x-1/2, -y+1, z$ ] $1.87$ $2.703(4)$ $148$ N(11)-H(11)O(201) [ $x+1/2, -y, z$ ] $2.27$ $3.080(5)$ $145$ N(11)-H(11)O(201) [ $x+1/2, y, z-1/2$ ] $2.45$ $3.039(4)$ $121$ N(8)-H(8)O(700) [ $-x+1/2, y, z-1/2$ ] $1.93$ $2.820(5)$ $159$ [Cu <sub>2</sub> (Hte3a)(H <sub>2</sub> O) <sub>3</sub> Cl]Cl <sub>0.5</sub> (ClO <sub>4</sub> ) <sub>0.5</sub> ·2H <sub>2</sub> O $5^d$ O(1)-H(B)O(181) [ $x+1/2, -y+1/2, z+1/2$ ] $1.86(5)$ $2.677(7)$ $170(6)$ O(2)-H(C)O(182) [ $x+1/2, -y+1/2, z+1/2$ ] $1.90(4)$ $2.726(8)$ $178(7)$ O(2)-H(D)Cl(1)[ $-x+1, -y, -z+2$ ] $2.46(6)$ $3.246(4)$ $159(6)$	$(H_7 te 3a1p)(ClO_4)_2.4.25H_2O 4^d$			
N(8)-H(8)···O(202)2.392.718(5)101N(11)-H(11)···O(222)2.322.720(5)106N(4)-H(4)···O(163) [ $x$ -1/2, $-y$ +1, $z$ ]1.872.703(4)148N(11)-H(11)···O(201) [ $x$ +1/2, $-y$ , $z$ ]2.273.080(5)145N(11)-H(11)···O(182) [ $-x$ -1/2, $y$ , $z$ -1/2 ]2.453.039(4)121N(8)-H(8)···O(700) [ $-x$ +1/2, $y$ , $z$ -1/2 ]1.932.820(5)159[Cu <sub>2</sub> (Hte3a)(H <sub>2</sub> O) <sub>3</sub> Cl]Cl <sub>0.5</sub> (ClO <sub>4</sub> ) <sub>0.5</sub> ·2H <sub>2</sub> O5 <sup>d</sup> O(1)-H(B)···O(181) [ $x$ +1/2, $-y$ +1/2, $z$ +1/2 ]1.86(5)2.677(7)170(6)O(2)-H(C)···O(182) [ $x$ +1/2, $-y$ +1/2, $z$ +1/2 ]1.90(4)2.726(8)178(7)O(2)-H(D)···Cl(1)[ $-x$ +1, $-y$ , $-z$ +2 ]2.46(6)3.246(4)159(6)O(2)-H(F)···O(202) [ $-x$ +1/2, $y$ -1/2, $-z$ +3/2 ]1.93(6)2.720(8)159(6)	$N(4)-H(4)\cdots O(182)$	2.19	2.720(4)	115
N(11)-H(11)···O(222)2.322.720(5)106N(4)-H(4)···O(163) [ $x$ -1/2, $-y$ +1, $z$ ]1.872.703(4)148N(11)-H(11)···O(201) [ $x$ +1/2, $-y$ , $z$ ]2.273.080(5)145N(11)-H(11)···O(182) [ $-x$ -1/2, $y$ , $z$ -1/2]2.453.039(4)121N(8)-H(8)···O(700) [ $-x$ +1/2, $y$ , $z$ -1/2]1.932.820(5)159[Cu <sub>2</sub> (Hte3a)(H <sub>2</sub> O) <sub>3</sub> Cl]Cl <sub>0.5</sub> (ClO <sub>4</sub> ) <sub>0.5</sub> ·2H <sub>2</sub> O5 <sup>d</sup> O(1)-H(B)···O(181) [ $x$ +1/2, $-y$ +1/2, $z$ +1/2]1.86(5)2.677(7)170(6)O(2)-H(C)···O(182) [ $x$ +1/2, $-y$ +1/2, $z$ +1/2]1.90(4)2.726(8)178(7)O(2)-H(D)···Cl(1)[ $-x$ +1, $-y$ , $-z$ +2]2.46(6)3.246(4)159(6)O(2)-H(F)···O(202) [ $-x$ +1/2, $y$ -1/2, $-z$ +3/2]1.93(6)2.720(8)159(6)	N(8)–H(8)····O(202)	2.39	2.718(5)	101
N(4)-H(4)···O(163) [ $x-1/2$ , $-y+1$ , $z$ ]1.872.703(4)148N(11)-H(11)···O(201) [ $x+1/2$ , $-y$ , $z$ ]2.273.080(5)145N(11)-H(11)···O(182) [ $-x-1/2$ , $y$ , $z-1/2$ ]2.453.039(4)121N(8)-H(8)···O(700) [ $-x+1/2$ , $y$ , $z-1/2$ ]1.932.820(5)159[Cu <sub>2</sub> (Hte3a)(H <sub>2</sub> O) <sub>3</sub> Cl]Cl <sub>0.5</sub> (ClO <sub>4</sub> ) <sub>0.5</sub> ·2H <sub>2</sub> O5 <sup>d</sup> O(1)-H(B)···O(181) [ $x+1/2$ , $-y+1/2$ , $z+1/2$ ]1.86(5)2.677(7)170(6)O(2)-H(C)···O(182) [ $x+1/2$ , $-y+1/2$ , $z+1/2$ ]1.90(4)2.726(8)178(7)O(2)-H(D)···Cl(1)[ $-x+1$ , $-y$ , $-z+2$ ]2.46(6)3.246(4)159(6)O(2)-H(F)···O(202) [ $-x+1/2$ , $y-1/2$ , $-z+3/2$ ]1.93(6)2.720(8)159(6)	$N(11)-H(11)\cdotsO(222)$	2.32	2.720(5)	106
N(11)-H(11)···O(201) [ $x+1/2$ , - $y$ , $z$ ]2.273.080(5)145N(11)-H(11)···O(182) [ $-x-1/2$ , $y$ , $z-1/2$ ]2.453.039(4)121N(8)-H(8)···O(700) [ $-x+1/2$ , $y$ , $z-1/2$ ]1.932.820(5)159[Cu <sub>2</sub> (Hte3a)(H <sub>2</sub> O) <sub>3</sub> Cl]Cl <sub>0.5</sub> (ClO <sub>4</sub> ) <sub>0.5</sub> ·2H <sub>2</sub> O5 <sup>d</sup> O(1)-H(B)···O(181) [ $x+1/2$ , $-y+1/2$ , $z+1/2$ ]1.86(5)2.677(7)170(6)O(2)-H(C)···O(182) [ $x+1/2$ , $-y+1/2$ , $z+1/2$ ]1.90(4)2.726(8)178(7)O(2)-H(D)···Cl(1)[ $-x+1$ , $-y$ , $-z+2$ ]2.46(6)3.246(4)159(6)O(2)-H(F)···O(202) [ $-x+1/2$ , $y-1/2$ , $-z+3/2$ ]1.93(6)2.720(8)159(6)	$N(4)-H(4)\cdots O(163) [x-1/2, -y+1, z]$	1.87	2.703(4)	148
N(11)-H(11)···O(182) [ -x-1/2, y, z-1/2 ]2.45 $3.039(4)$ 121N(8)-H(8)···O(700) [ -x+1/2, y, z-1/2 ]1.932.820(5)159[Cu <sub>2</sub> (Hte3a)(H <sub>2</sub> O) <sub>3</sub> Cl]Cl <sub>0.5</sub> (ClO <sub>4</sub> ) <sub>0.5</sub> ·2H <sub>2</sub> O <b>5</b> <sup>d</sup> O(1)-H(B)···O(181) [ x+1/2, -y+1/2, z+1/2 ]1.86(5)2.677(7)170(6)O(2)-H(C)···O(182) [ x+1/2, -y+1/2, z+1/2 ]1.90(4)2.726(8)178(7)O(2)-H(D)···Cl(1)[ -x+1, -y, -z+2 ]2.46(6)3.246(4)159(6)O(2)-H(F)···O(202) [ -x+1/2, y-1/2, -z+3/2 ]1.93(6)2.720(8)159(6)	N(11)–H(11)····O(201) [ $x+1/2, -y, z$ ]	2.27	3.080(5)	145
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(11)–H(11)····O(182) [-x-1/2, y, z-1/2]	2.45	3.039(4)	121
$\begin{bmatrix} Cu_{2}(Hte3a)(H_{2}O)_{3}Cl]Cl_{0.5}(ClO_{4})_{0.5} \cdot 2H_{2}O  5^{d} \\ O(1)-H(B)\cdots O(181) \begin{bmatrix} x+1/2, -y+1/2, z+1/2 \end{bmatrix} & 1.86(5) & 2.677(7) & 170(6) \\ O(2)-H(C)\cdots O(182) \begin{bmatrix} x+1/2, -y+1/2, z+1/2 \end{bmatrix} & 1.90(4) & 2.726(8) & 178(7) \\ O(2)-H(D)\cdots Cl(1) \begin{bmatrix} -x+1, -y, -z+2 \end{bmatrix} & 2.46(6) & 3.246(4) & 159(6) \\ O(2)-H(F)\cdots O(202) \begin{bmatrix} -x+1/2, y-1/2, -z+3/2 \end{bmatrix} & 1.93(6) & 2.720(8) & 159(6) \\ \end{bmatrix}$	N(8)–H(8)····O(700) [ - <i>x</i> +1/2, <i>y</i> , <i>z</i> -1/2 ]	1.93	2.820(5)	159
$O(1)-H(B)\cdots O(181) [x+1/2, -y+1/2, z+1/2]$ $1.86(5)$ $2.677(7)$ $170(6)$ $O(2)-H(C)\cdots O(182) [x+1/2, -y+1/2, z+1/2]$ $1.90(4)$ $2.726(8)$ $178(7)$ $O(2)-H(D)\cdots Cl(1)[-x+1, -y, -z+2]$ $2.46(6)$ $3.246(4)$ $159(6)$ $O(2)-H(F)\cdots O(202) [-x+1/2, y-1/2, -z+3/2]$ $1.93(6)$ $2.720(8)$ $159(6)$	$[Cu_2(Hte3a)(H_2O)_3Cl]Cl_{0.5}(ClO_4)_{0.5} \cdot 2H_2O 5^d$			
O(1)-H(D) $O(101)$ [ $x$ +H/2, $y$ +H/2, $z$ +H/2 ] $1.00(3)$ $2.077(7)$ $170(0)$ $O(2)$ -H(C) $O(182)$ [ $x$ +H/2, $-y$ +H/2, $z$ +H/2 ] $1.90(4)$ $2.726(8)$ $178(7)$ $O(2)$ -H(D) $O(10)$ [ $-x$ +1, $-y$ , $-z$ +2 ] $2.46(6)$ $3.246(4)$ $159(6)$ $O(2)$ -H(F) $O(202)$ [ $-x$ +H/2, $y$ -H/2, $-z$ +3/2 ] $1.93(6)$ $2.720(8)$ $159(6)$	O(1) = H(B) = O(181) [r + 1/2 - v + 1/2 - r + 1/2]	1.86(5)	2677(7)	170(6)
$\begin{array}{c} O(2) - H(C) - O(102) \left[ x + 1/2, y + 1/2, z + 1/2 \right] \\ O(2) - H(D) \cdots Cl(1) \left[ -x + 1, -y, -z + 2 \right] \\ O(2) - H(F) \cdots O(202) \left[ -x + 1/2, y - 1/2, -z + 3/2 \right] \\ \end{array}$	O(2) = H(C) O(182) [x+1/2, -y+1/2, z+1/2]	1.00(3)	2.077(7)	178(7)
O(2) - H(E) - O(202) [-x+1/2, y-1/2, -z+3/2] 1.93(6) 2.720(8) 159(6)	$O(2) = H(D) \cdots C[(1)[-r+1] - v - 7+2]$	2 46(6)	3.726(0)	159(6)
	$O(2)-H(F)\cdots O(202)$ [-x+1/2, y-1/2, -z+3/2]	1.93(6)	2.720(8)	159(6)

Table S1 Hydrogen bond dimensions found in solid state for the compounds 1–5

<sup>*a*</sup> A, D denote the proton acceptor and donor, respectively; <sup>*b*</sup> and <sup>*c*</sup> correspond to the hydrogen dimensions found for the first and second molecule of **2**, respectively; <sup>*d*</sup> the hydrogen bonds involving disordered water molecules are not quoted.

Species HL	H₅te3a1p	H <sub>3</sub> te3a	H <sub>4</sub> teta <sup>b</sup>	H <sub>8</sub> tetp <sup>b</sup>
11	11.78(1) <sup>c</sup>	11.91(2)	10.59	-
12	21.66(1)	21.14(2)	20.68	25.28
13	28.00(1)	24.87(3)	24.80	34.13
14	31.85(1)	27.81(3)	28.09	41.81
15	34.48(2)	29.80(7)	29.9	48.04
16	36.62(2)	-	-	53.37
17	-	-	-	55.65

**Table S2** Protonation constants  $(\log \beta_{HL})^a$  of the studied ligands determined by potentiometry; T = 298.2 K; I = 0.10 mol dm<sup>-3</sup> in NMe<sub>4</sub>NO<sub>3</sub>

<sup>*a*</sup> Values in brackets are standard deviations in the last significant figure. <sup>*b*</sup> From refs. 1 and 2. <sup>*c*</sup> Determined by <sup>31</sup>P NMR spectroscopy.

**Table S2** Stability constants  $(\log \beta_{MHL})^a$  of complexes of the studied ligands with some divalent metal ions determined by potentiometry. T = 298.2 K; I = 0.10 mol dm<sup>-3</sup> in NMe<sub>4</sub>NO<sub>3</sub>

Ion	Species MHL	H₅te3a1p	H <sub>3</sub> te3a	H₄teta	H <sub>8</sub> tetp
Ca <sup>2+</sup>	101	6.69(1)	5.08(2)	$8.4^b$	-
	111	15.42(2)	-	$15.6^{b}$	19.33
	1-11	-3.55(1)	-6.59(2)	-	-
	1-21	-15.29(2)	-	-	-
Mn <sup>2+</sup>	101	11.64(2)	12.56(2)	$11.3^{b}$	$10.8^{d}$
	111	19.26(2)	18.59(4)	-	-
	121	25.67(3)	24.40(4)	-	-
	131	31.12(3)	27.83(7)	-	-
	1-11	2.40(3)	2.37(2)	-	-
	1-21	-8.44(5)	-	-	-
Co <sup>2+</sup>	101	16.42(2)	19.53(2)	$16.6^{b}$	$15.3^{d}$
	111	23.74(1)	23.14(2)	$20.8^{b}$	-
	121	27.53(1)	-	$23.64^{b}$	-
	1-11	5.34(2)	7.48(4)	-	-
Ni <sup>2+</sup>	101	20.04(3)	20.19(2)	19.91 <sup>b</sup>	$15.6^{d}$
	111	27.26(2)	23.81(2)	$24.11^{b}$	-
	121	31.08(2)	-	27.31 <sup>b</sup>	-
	1-11	10.52(3)	9.34(3)	-	-
$Cu^{2+}$	101	21.58(3)	21.84(3)	21.07(2) <sup>e</sup>	25.99(8) <sup>e</sup>
	111	28.43(1)	25.08(3)	$24.51(2)^{e}$	34.08(7) <sup>e</sup>
	121	31.79(1)	-	26.98(3) <sup>e</sup>	41.01(7) <sup>e</sup>
	131	-	-	-	46.90(7) <sup>e</sup>
	141	-	-	-	51.93(4) <sup>e</sup>
	1-11	10.30(3)	9.93(4)	-	-
$Zn^{2+}$	101	18.16(3)	19.63(1)	17.48(4) <sup>f</sup>	18.31(4) <sup>f</sup>
	111	25.31(1)	23.09(1)	21.64(4)	27.44(4)
	121	28.84(2)	-	25.01(4)	34.63(4)
	131	-	-	-	41.29(3)
	141	-	-	-	46.79(3)
	1-11	6.95(4)	7.56(3)	6.68(6)	7.22(5)
$Cd^{2+}$	101	17.90(2)	18.14(1)	$18.0^{b}$	$16.7^{d}$
	111	25.22(1)	21.71(1)	$22.04^{b}$	-
	121	28.81(1)	24.28(7)	$24.44^{c}$	-
	1-11	8.34(3)	7.37(2)	-	-
	1-21	-2.82(3)	-	-	-
$Pb^{2+}$	101	13.58(4)	13.53(1)	$14.3^{b}$	$15.5^{d}$
	111	21.66(3)	19.25(2)	$19.05^{b}$	-
	121	26.93(2)	24.42(1)	23.3 <sup>b</sup>	-
	131	30.81(7)	27.81(3)	-	-
	1-11	3.72(4)	2.83(1)	-	-
	1-21	-8.43(9)	-	-	-

<sup>*a*</sup> Values in brackets are standard deviations in the last significant figure. <sup>*b*</sup> From ref. 3. <sup>*c*</sup> From ref. 4; the value in ref. 3 is incorrect. <sup>*d*</sup> From ref. 5. <sup>*e*</sup> Previously cited in ref. 1. <sup>*f*</sup> Previously cited in ref. 6.

Metal	pН	Ligand resonance (ppm)	Complex resonance(s) (ppm)
	2.94	13.06	-
	6.47	13.85	14.20, 15.08
$Zn^{2+}$	7.97	6.90	12.63, 13.43
	8.78	6.58	12.36, 13.15
	10.50	7.08	12.33, 13.11
	2.50	11.92	16.75
$\mathrm{Cd}^{2+}$	5.73	14.17	16.48
	8.60	6.64	14.39

Table S3 Peak assignment of the  ${}^{31}$ P NMR spectra of zinc(II) and cadmium(II) complexes of H<sub>5</sub>te3a1p at different pH values in water solution



Fig. S1 Species distribution diagram for  $H_5$ te3a1p at  $1 \times 10^{-3}$  mol dm<sup>-3</sup>.



Fig. S2 Species distribution diagram for  $H_3$ te3a at  $1 \times 10^{-3}$  mol dm<sup>-3</sup>.



Fig. S3 Species distribution diagram for  $Cu^{2+}$ -H<sub>5</sub>te3a1p at  $C_M = C_L = 1 \times 10^{-3} \text{ mol dm}^{-3}$ .



**Fig. S4** Species distribution diagram for  $Cu^{2+}$ -H<sub>3</sub>te3a at  $C_M = C_L = 1 \times 10^{-3}$  mol dm<sup>-3</sup>.



**Fig. S5** Species distribution diagram for an equimolar mixture of  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$  and  $H_3$ te3a at  $1 \times 10^{-1}$  mol dm<sup>-3</sup>. The amount of free ligand and metal complexes is expressed as the sum of all of their protonated species in percentage relative to the initial amount of  $H_3$ te3a.

#### References

- 1. R. Delgado, J. Costa, K. P. Guerra and L. M. P. Lima, Pure Appl. Chem., 2005, 3, 569-579.
- F. Marques, L. Gano, M. P. Campello, S. Lacerda, I. Santos, L. M. P. Lima, J. Costa, P. Antunes and R. Delgado, *J. Inorg. Biochem.*, 2006, 100, 270-280.
- G. Anderegg, F. Arnaud-Neu, R. Delgado, J. Felcman and K. Popov, *Pure Appl. Chem.*, 2005, 77, 1445-1495.
- 4. S. Chaves, R. Delgado and J. J. R. Fraústo da Silva, *Talanta*, 1992, **39**, 249-254.
- 5. M.I. Kabachnik and Y. M. Polikarpov, Zh. Obsch. Khim (USSR), 1988, 58, 1937-1962.
- 6. R. Delgado, V. Félix, L. M. P. Lima and D. W. Price, Dalton Trans., 2007, 2734-2745.