

## Supplementary data

### Desulfurization processes of thiosemicarbazonecopper(II) derivatives in acid and basic aqueous media.

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#### FIGURES

- Figure S1.** H–bonds for compounds **1** (a), **2** (b), **3** (c,d), **4** (e) and **5** (f). Hydrogen atoms of compound **2** have been omitted for clarity.
- Figure S2.**  $\pi$ – $\pi$  stacking for compounds **1** (a), **2** (b), **3** (c) and **4** and **5** (d).
- Figure S3.** Anion– $\pi$  interactions in compounds **4** (a) and **5** (b).
- Figure S4.** Proposed species for the FAB<sup>+</sup> spectra of compounds obtained after refluxing treatment.
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- Figure S8.** FT-IR spectra of compound [{Cu(L')(NO<sub>3</sub>)<sub>2</sub>}] and the solid obtained after refluxing treatment of [{Cu(L')(NO<sub>3</sub>)<sub>2</sub>}] (a).
- Figure S9.** FT-IR spectra of compound [CuL<sub>2</sub>] and the solid obtained after refluxing treatment of [CuL<sub>2</sub>] (a).
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- Figure S12.** FT-IR spectra of compounds CoL<sub>2</sub>(NO<sub>3</sub>), ZnL<sub>2</sub>(H<sub>2</sub>O) and PbL(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>0.5</sub>.
- Figure S13.** FT-IR spectrum of compound **1**.
- Figure S14.** FT-IR spectrum of compounds **2** and **2a**.

**Figure S15.** FT-IR spectrum of compound **3**.

**Figure S16.** FT-IR spectra of compounds **4** and **5**.

**Figure S17.** X-band EPR spectrum of compound **2a** at 290K. Experimental details: modulation frequency = 100 kHz, modulation amplitude = 1 G, time constant = 40.96 ms, conversion time = 327.68 ms, gain =  $2 \times 10^4$ , power = 2.0 mW, microwave frequency = 9.7753 GHz. Fitting parameters: Lorentzian-type signal,  $g_1 = 2.184$  (linewidth  $H_1 = 41$  G),  $g_2 = 2.061$  ( $H_2 = 26$  G),  $g_3 = 2.046$  ( $H_3 = 24$  G).

**Figure S18.** X-band EPR spectrum of compound **4** at 290K. Experimental details: modulation frequency = 100 kHz, modulation amplitude = 1 G, time constant = 40.96 ms, conversion time = 163.84 ms, gain =  $2 \times 10^4$ , power = 0.2 mW, microwave frequency = 9.7751 GHz. Fitting parameters: Lorentzian-type signal,  $g_{||} = 2.201$ , (linewidth  $H_{||} = 40$  G),  $g_{\perp} = 2.048$ , ( $H_{\perp} = 29$  G).

## TABLES

**Table S1.** Selected distances (Å) and angles (°) of H–bonds study.

**Table S2.** Selected parameters for the  $\pi$ – $\pi$  stacking study.

**Table S3.** Selected parameters for the anion– $\pi$  study.

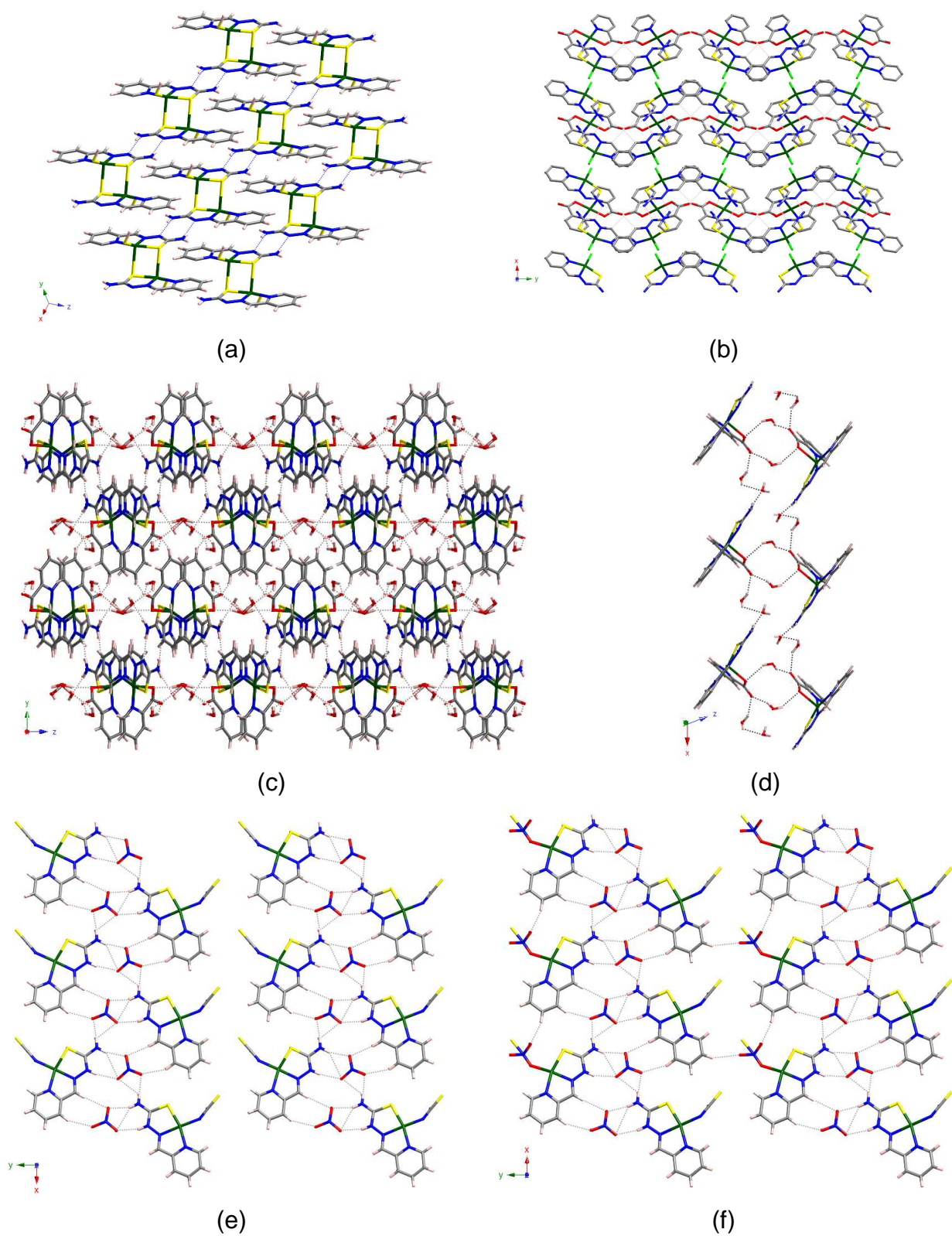
**Table S4.** Most important peaks of ESI mass spectra of  $\text{CuL}(\text{NO}_3)$  aqueous solutions at different pH values after 1 hour.

**Table S5.** Most important peaks of ESI mass spectra of  $[\{\text{Cu}(\text{L}')(\text{NO}_3)\}_2]$  aqueous solutions at different pH values after 1 hour.

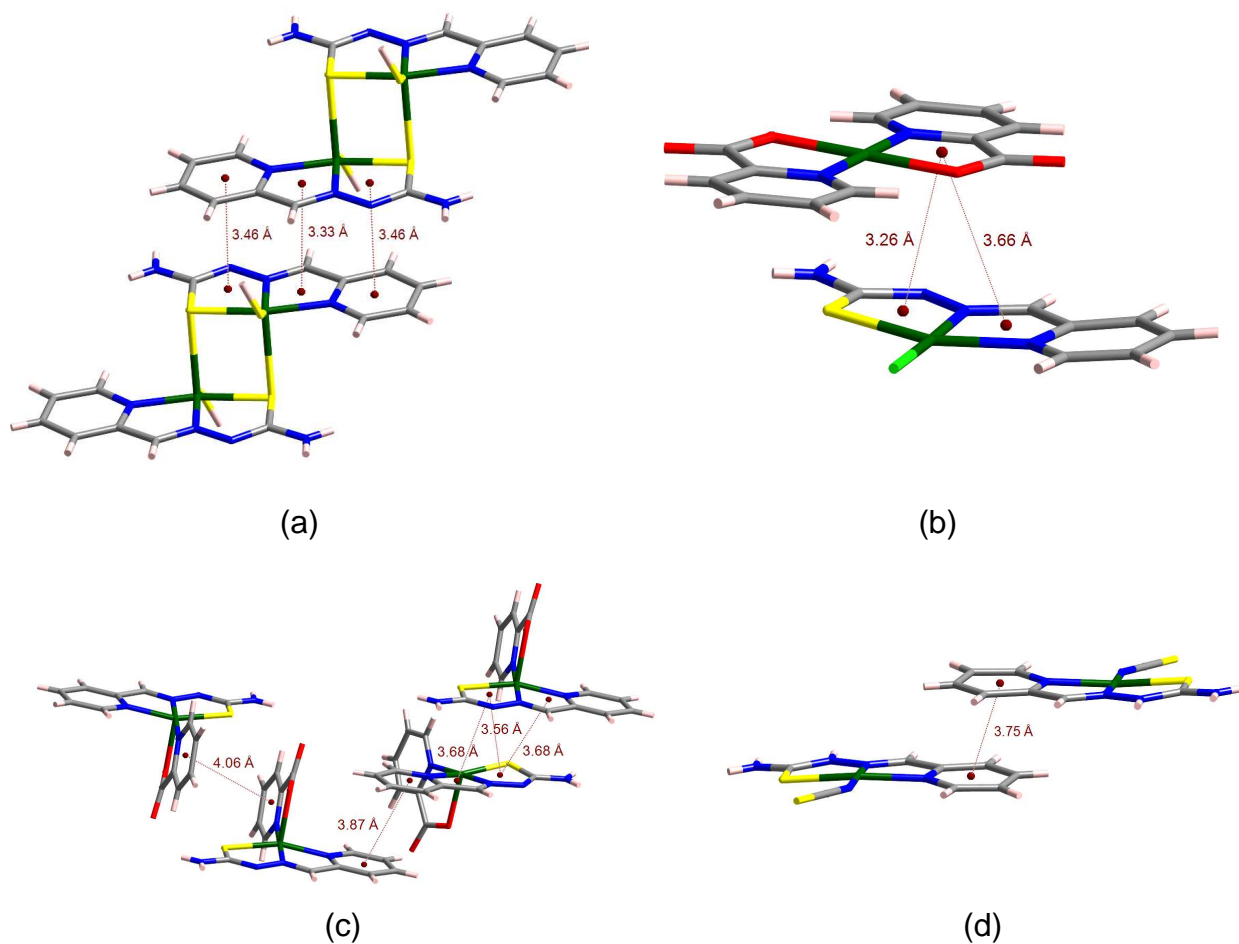
**Table S6.** Most important peaks of ESI mass spectra of  $\text{FeL}_2(\text{NO}_3)(\text{H}_2\text{O})$  aqueous solution without any pH adjustment after 1 hour.

**Table S7.** Aqua ions standard reduction potentials (pH = 0, T = 25 °C and P = 1 atm) compared to the limit values for the water stability field.

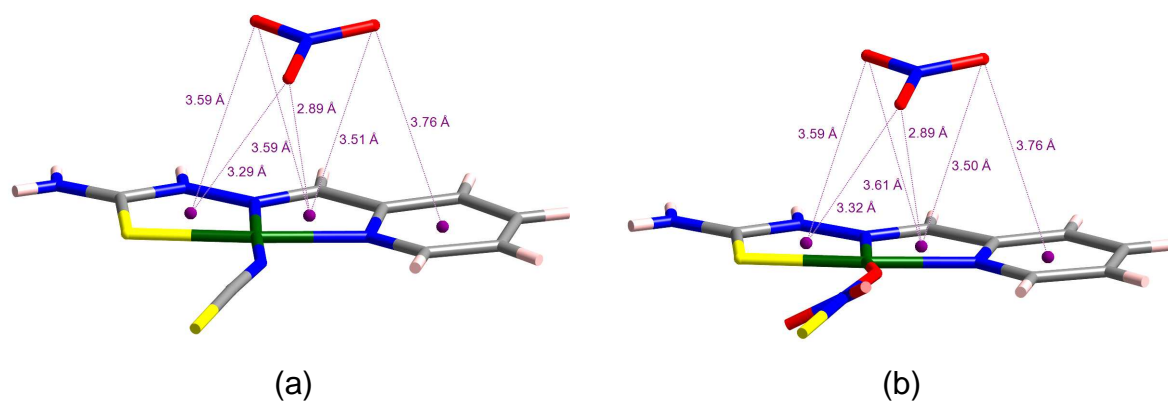
**Table S8.** Standard reduction potentials of some thiosemicarbazonometal complexes.



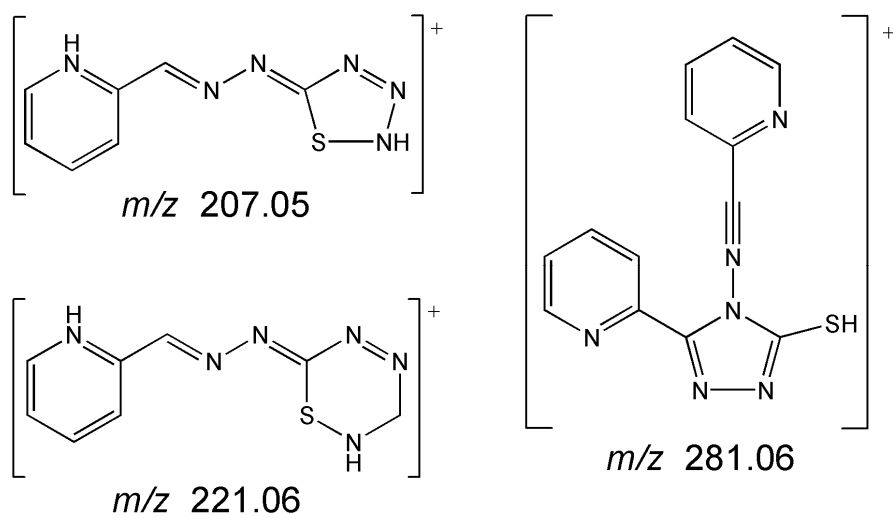
**Figure S1.** H-bonds for compounds **1** (a), **2** (b), **3** (c,d), **4** (e) and **5** (f). Hydrogen atoms of compound **2** have been omitted for clarity.



**Figure S2.**  $\pi$ - $\pi$  stacking for compounds **1** (a), **2** (b), **3** (c) and **4** and **5** (d).

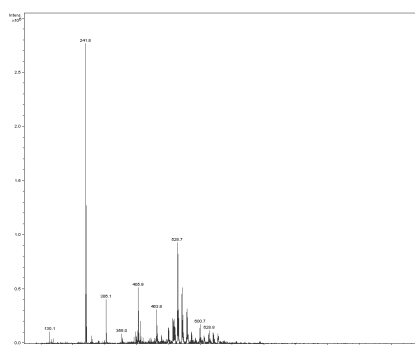


**Figure S3.** Anion- $\pi$  interactions in compounds **4** (a) and **5** (b).

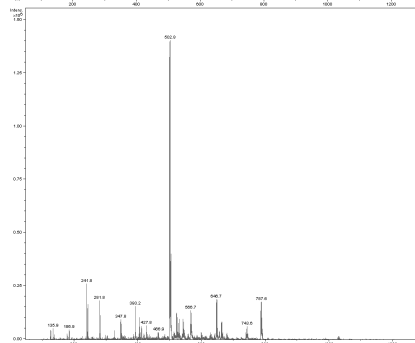


**Figure S4.** Proposed species for the FAB<sup>+</sup> spectra of compounds obtained after refluxing treatment.

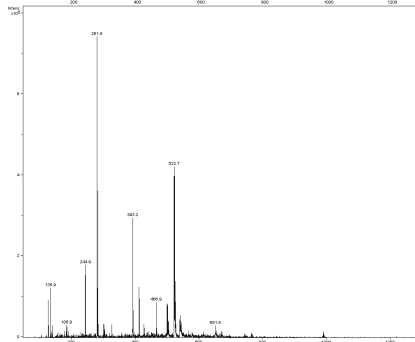
Without any pH adjustment



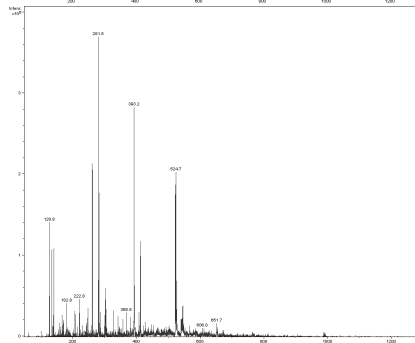
pH = 7.4



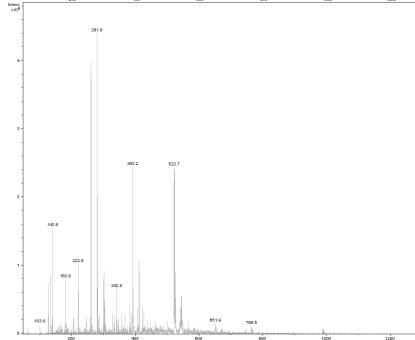
pH = 9.0



pH = 11.0

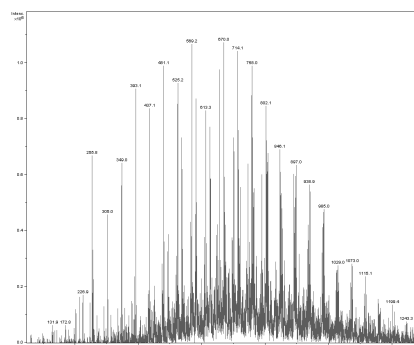


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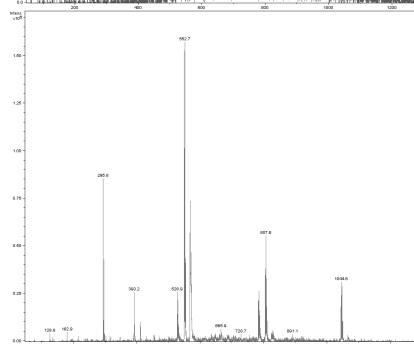


**Figure S5.** ESI spectra of  $\text{CuL}(\text{NO}_3)$  aqueous solutions at different pH values after 1 hour.

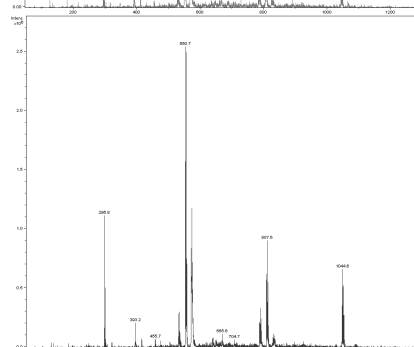
Without any pH adjustment



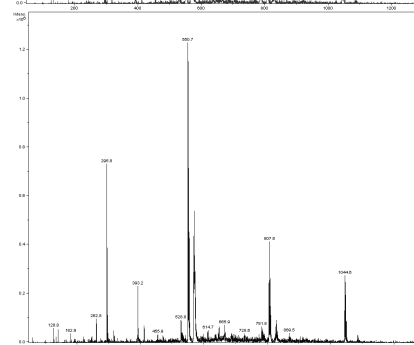
pH = 7.4



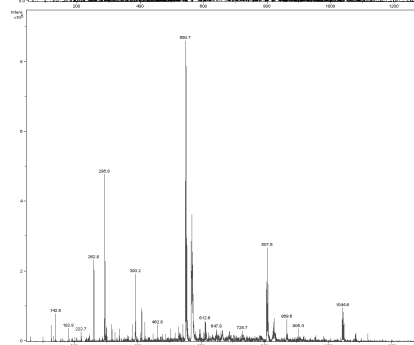
pH = 9.0



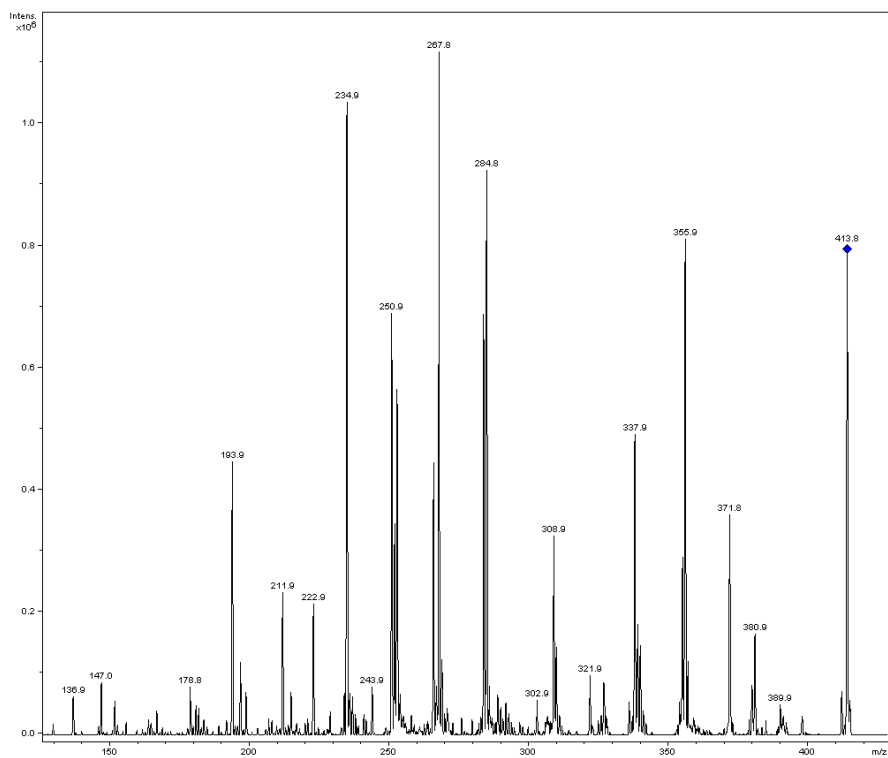
pH = 11.0



pH = 13.0

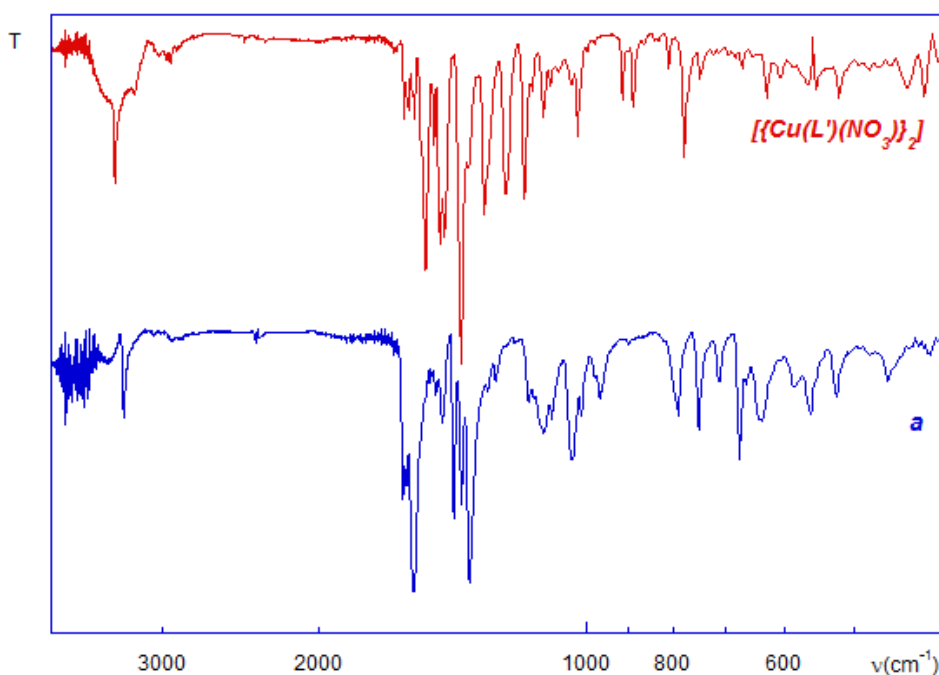


**Figure S6.** ESI spectra of  $[\{\text{Cu}(\text{L}')(\text{NO}_3)\}_2]$  aqueous solutions at different pH values after 1 hour.

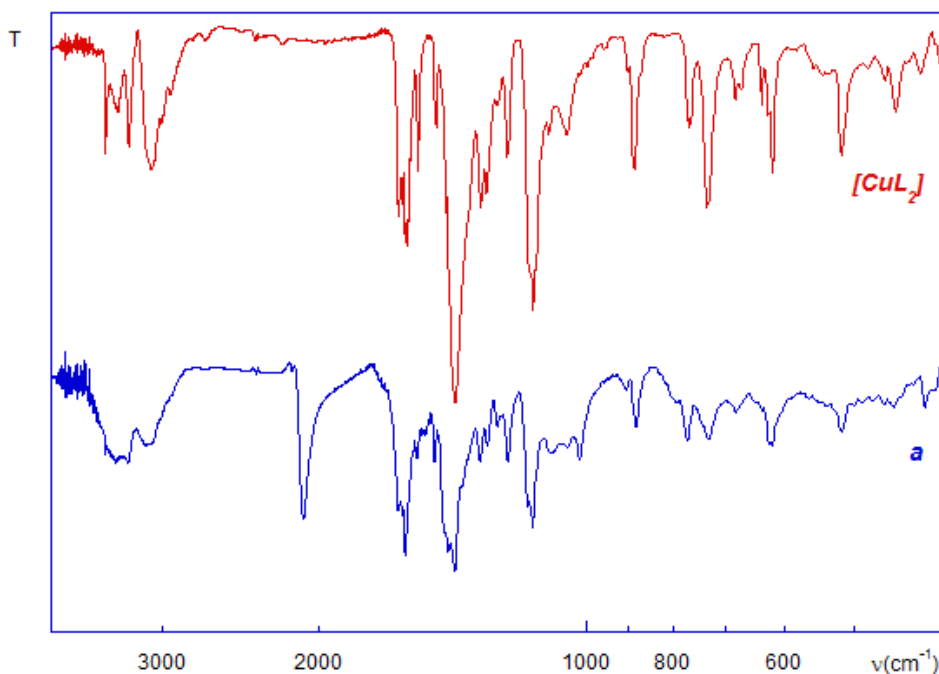


**Figure S7.** ESI spectra of  $\text{FeL}_2(\text{NO}_3)(\text{H}_2\text{O})$  aqueous solutions without any pH adjustment after 1 hour.

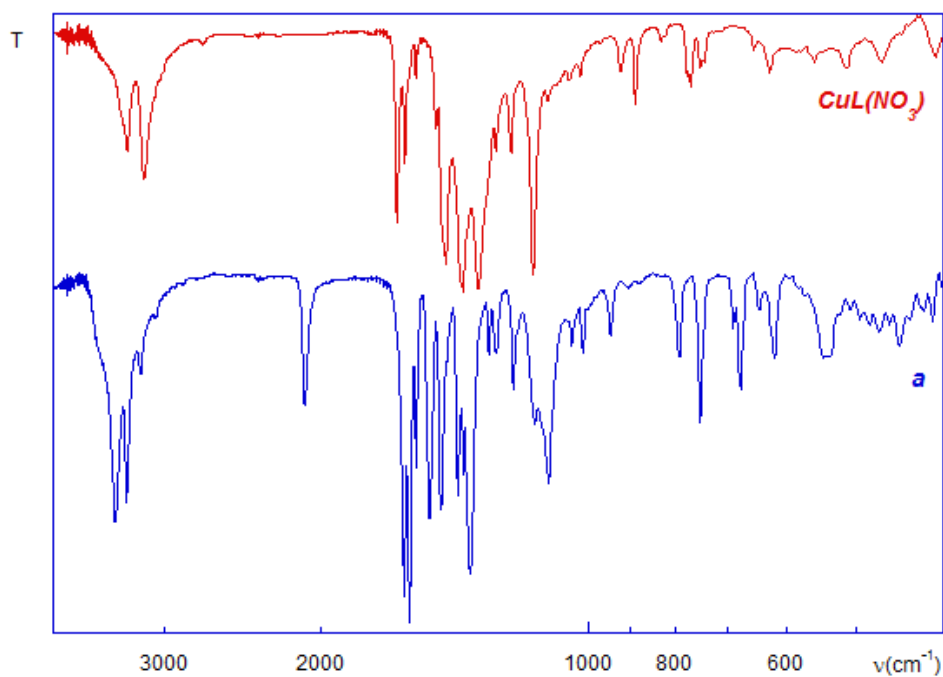




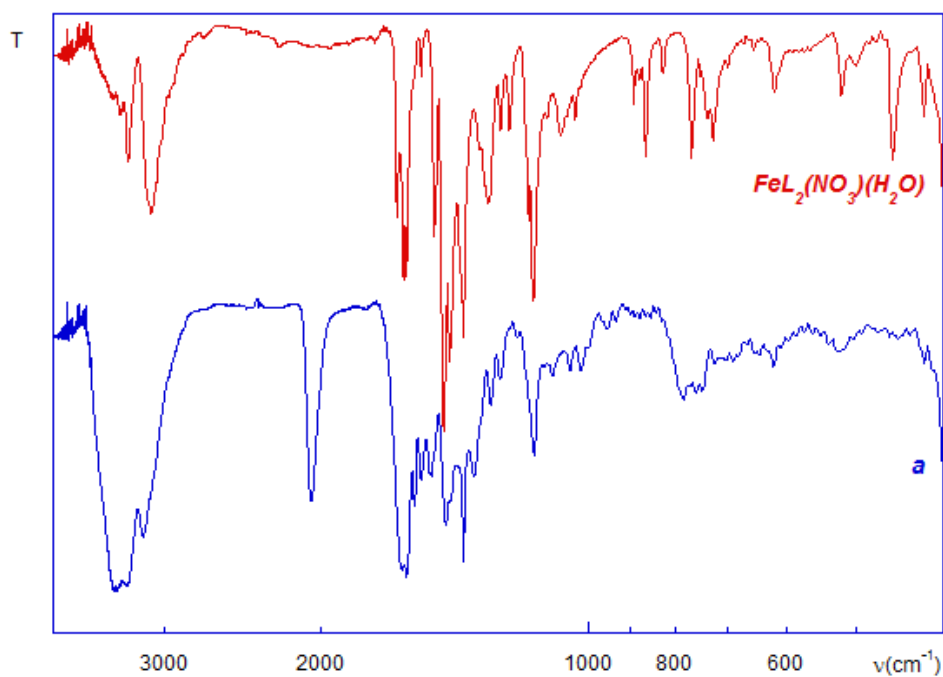
**Figure S8.** FT-IR spectra of compound  $[\text{Cu}(\text{L}')(\text{NO}_3)_2]$  and the solid obtained after refluxing treatment of  $[\text{Cu}(\text{L}')(\text{NO}_3)_2]$  (a).



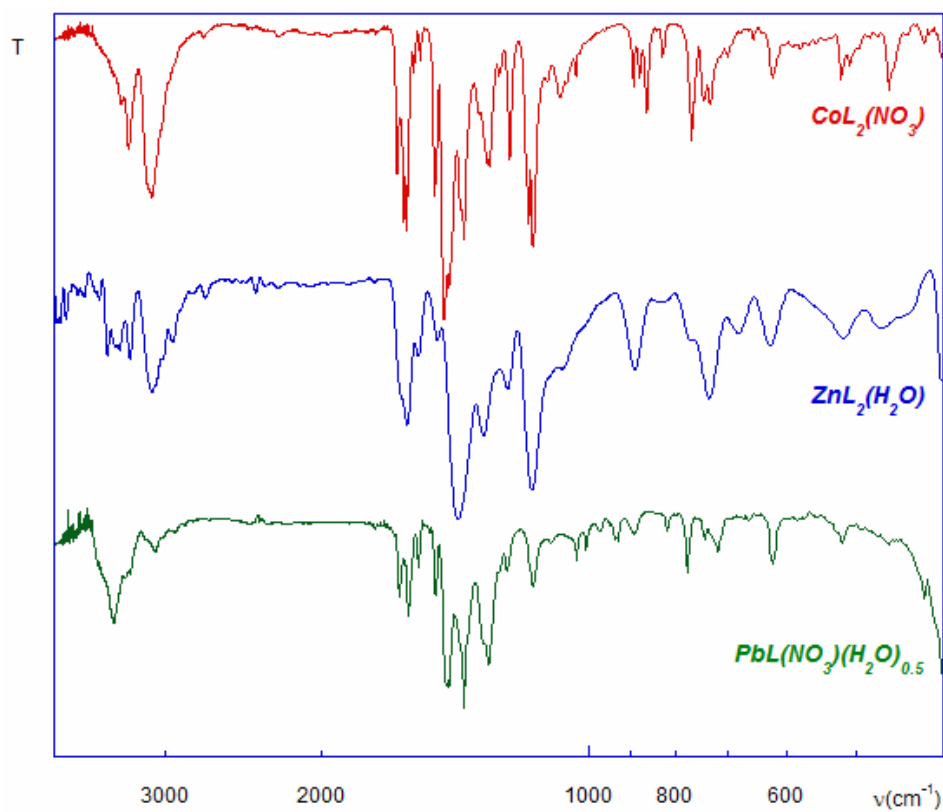
**Figure S9.** FT-IR spectra of compound  $[\text{CuL}_2]$  and the solid obtained after refluxing treatment of  $[\text{CuL}_2]$  (a).



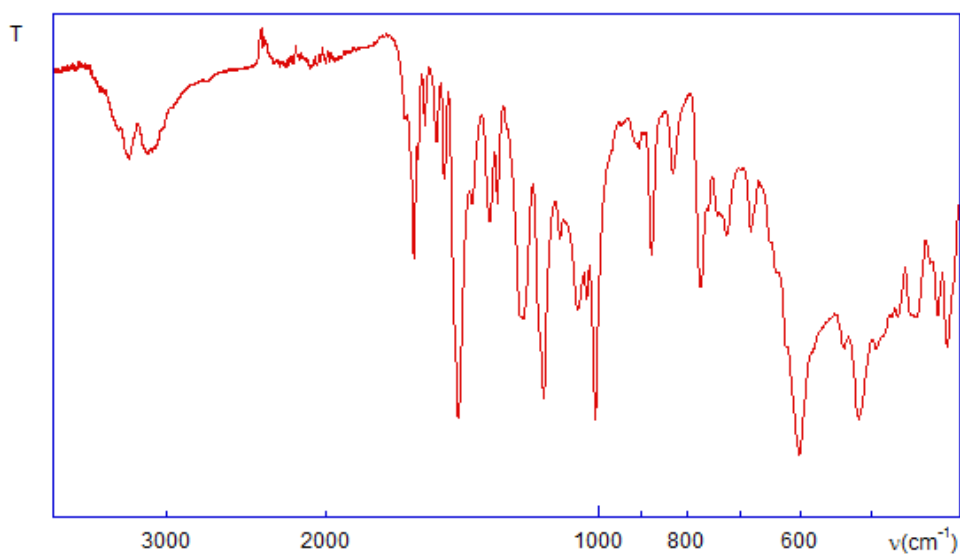
**Figure S10.** FT-IR spectra of compound  $CuL(NO_3)$  and the solid obtained after refluxing treatment of  $CuL(NO_3)$  (a).



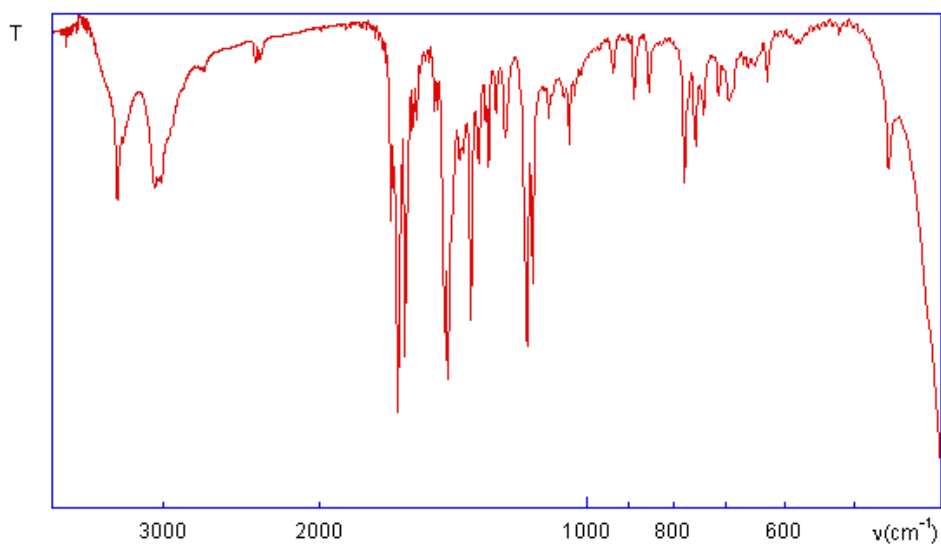
**Figure S11.** FT-IR spectra of compound  $FeL_2(NO_3)(H_2O)$  and the solid obtained after refluxing treatment of  $FeL_2(NO_3)(H_2O)$  (a).



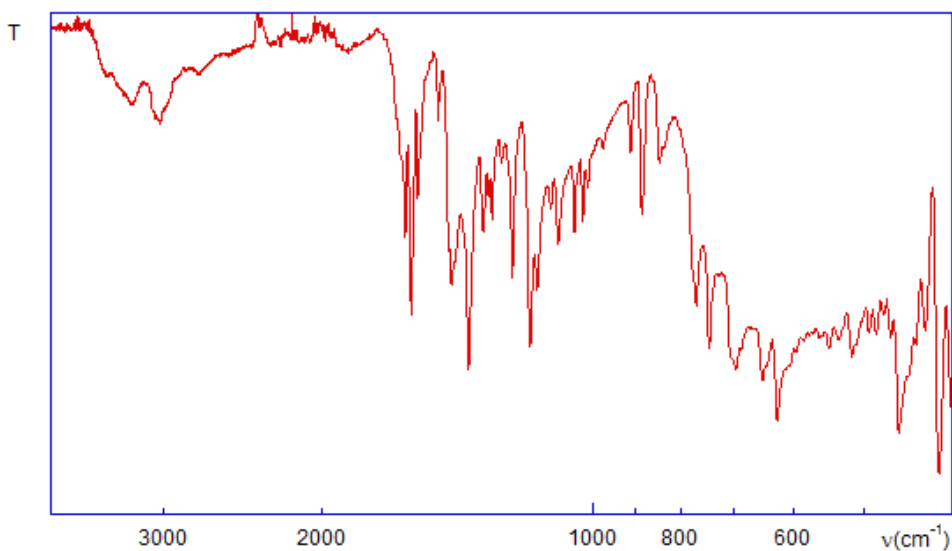
**Figure S12.** FT-IR spectra of compounds  $\text{CoL}_2(\text{NO}_3)$ ,  $\text{ZnL}_2(\text{H}_2\text{O})$  and  $\text{PbL}(\text{NO}_3)(\text{H}_2\text{O})_{0.5}$ .



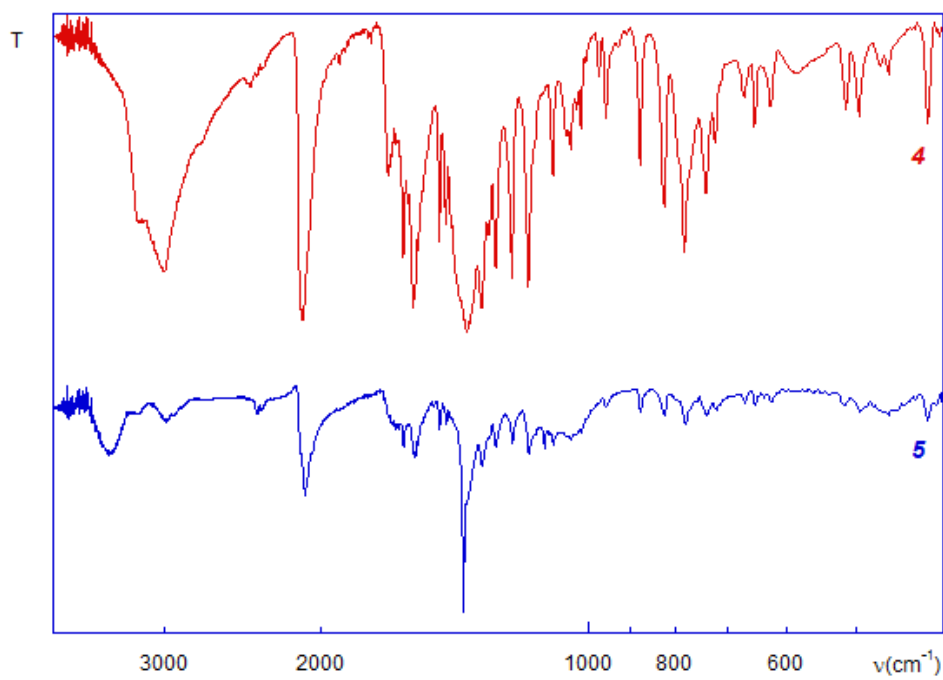
**Figure S13.** ATR FT-IR spectrum of compound 1.



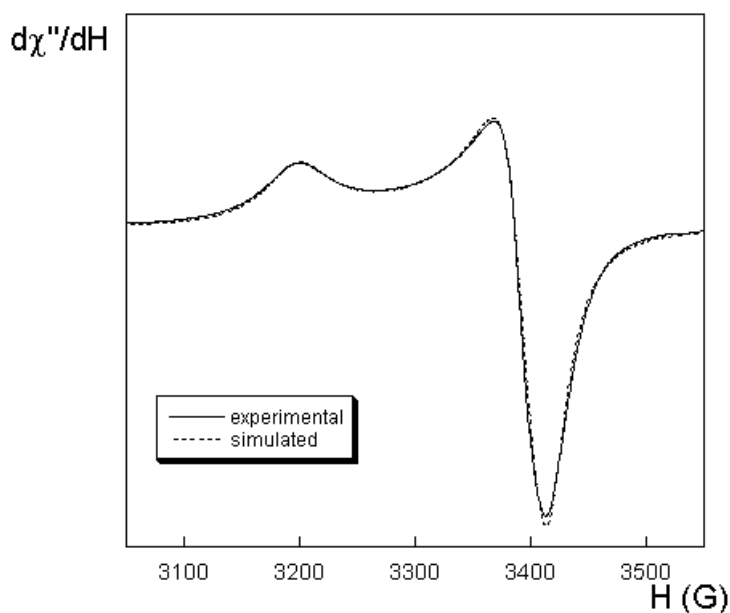
**Figure S14.** FT-IR spectrum of compounds **2** and **2a**.



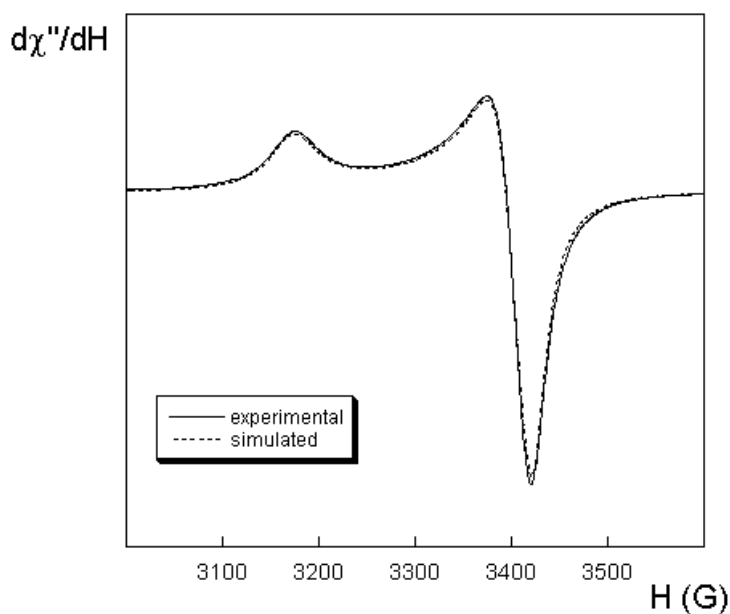
**Figure S15.** ATR FT-IR spectrum of compound **3**.



**Figure S16.** FT-IR spectra of compounds **4** and **5**.



**Figure S17.** X-band EPR spectrum of compound **2a** at 290K. Experimental details: modulation frequency = 100 kHz, modulation amplitude = 1 G, time constant = 40.96 ms, conversion time = 327.68 ms, gain =  $2 \times 10^4$ , power = 2.0 mW, microwave frequency = 9.7753 GHz. Fitting parameters: Lorentzian-type signal,  $g_1 = 2.184$  (linewidth  $H_1 = 41$  G),  $g_2 = 2.061$  ( $H_2 = 26$  G),  $g_3 = 2.046$  ( $H_3 = 24$  G).



**Figure S18.** X-band EPR spectrum of compound **4** at 290K. Experimental details: modulation frequency = 100 kHz, modulation amplitude = 1 G, time constant = 40.96 ms, conversion time = 163.84 ms, gain =  $2 \times 10^4$ , power = 0.2 mW, microwave frequency = 9.7751 GHz. Fitting parameters: Lorentzian-type signal,  $g_{||} = 2.201$ , (linewidth  $H_{||} = 40$  G),  $g_{\perp} = 2.048$ , ( $H_{\perp} = 29$  G).

**Table S1.** Selected distances (Å) and angles (°) of H-bonds study.

Compound	D–H...A	d (D–H)	d (H...A)	d (D...A)	∠ (DHA)
<b>1</b>	N4–H4A...N3 <sup>i</sup>	0.88	2.19	3.054(9)	167.3
<b>2</b>	N4–H4A...N3 <sup>ii</sup>	0.86	2.09	2.945(1)	176.2
	N4–H4B...O2 <sup>iii</sup>	0.86	2.17	2.873(1)	138.6
	C6–H6...O2 <sup>iv</sup>	0.93	2.33	3.250(2)	171.8
<b>3</b>	O2W–H1W2...O1W	0.85	2.21	2.821(1)	128.2
	N4–H4A...N3 <sup>v</sup>	0.86	2.10	2.955(1)	175.3
	N4–H4B...O1W <sup>vi</sup>	0.86	2.13	2.990(1)	174.6
	O2W–H2W2...O2 <sup>vii</sup>	0.85	2.18	2.911(1)	144.8
	O3W–H2W3...O2 <sup>vii</sup>	0.85	1.97	2.778(1)	158.5
	C9–H9...O2 <sup>viii</sup>	0.93	2.37	3.292(1)	171.5
	O3W–H1W3...O1 <sup>ix</sup>	0.85	2.30	3.045(1)	146.6
<b>4</b>	C41–H41...O11 <sup>x</sup>	0.93	2.34	3.22(2)	157.0
	C61–H61...O31 <sup>x</sup>	0.93	2.50	3.40(2)	165.3
	N32–H32A...O21 <sup>xi</sup>	0.86	2.03	2.849(14)	157.9
	N42–H42A...O31 <sup>xi</sup>	0.86	1.95	2.758(16)	156.6
	N42–H42A...O21 <sup>xi</sup>	0.86	2.40	3.129(16)	142.9
	N42–H42B...O22 <sup>xii</sup>	0.86	2.02	2.872(19)	173.0
	N42–H42B...O12 <sup>xii</sup>	0.86	2.65	3.211(18)	124.0
	N41–H41A...O32 <sup>xiii</sup>	0.86	1.93	2.773(16)	166.0
	N31–H31A...O12 <sup>xiii</sup>	0.86	2.07	2.912(15)	166.7
	N41–H41B...O21 <sup>xiv</sup>	0.86	2.44	3.021(16)	125.5
	N41–H41B...O11 <sup>xiv</sup>	0.86	1.97	2.814(18)	168.1
	C42–H42...O22 <sup>xv</sup>	0.93	2.36	3.22(2)	153.6
	C62–H62...O32 <sup>xv</sup>	0.93	2.32	3.24(2)	173.0
	<b>5</b>	C41–H41...O11	0.93	2.38	3.253(1)
C61–H61...O31		0.93	2.46	3.371(1)	167.4
N41–H41A...O32 <sup>xiii</sup>		0.86	1.96	2.806(1)	169.4
N31–H31A...O12 <sup>xiii</sup>		0.86	2.05	2.895(1)	167.2
C32–H32...O23 <sup>xi</sup>		0.93	2.48	3.349(1)	155.9
N41–H41B...O11 <sup>xi</sup>		0.86	1.95	2.794(1)	165.1
N41–H41B...O21 <sup>xi</sup>		0.86	2.45	2.994(1)	122.0
N32–H32A...O21 <sup>x</sup>		0.86	2.06	2.876(1)	157.7
N42–H42A...O21 <sup>x</sup>		0.86	2.46	3.182(1)	142.4
N42–H42A...O31 <sup>x</sup>		0.86	1.99	2.813(1)	160.6
C21–H21...O33 <sup>x</sup>		0.93	2.55	3.337(1)	143.0
N42–H42B...O12 <sup>xvi</sup>		0.86	2.71	3.236(1)	120.7
N42–H42B...O22 <sup>xvi</sup>		0.86	1.97	2.825(1)	170.4
C42–H42...O22 <sup>xvii</sup>		0.93	2.34	3.220(1)	157.5
C62–H62...O32 <sup>xvii</sup>		0.93	2.37	3.293(1)	175.3

(i = -x+2, -y+1, -z+2; ii = -x+2, -y, -z+2; iii = -x+3/2, y-1/2, -z+2; iv = x+1/2, -y+1/2, z; v = -x+1, -y, -z; vi = -x+1, y, -z+1/2; vii = -x, y, -z+1/2; viii = x+1/2, -y+1/2, z+1/2; ix = x, y, z+1; x = -x+1/2, y-1/2, -z+1/2; xi = x+1, y, z; xii = -x+1, -y+1, -z+1; xiii = x+1/2, -y+1/2, z-1/2; xiv = -x+3/2, y-1/2, -z+1/2; xv = -x+2, -y+1, -z+1; xvi = -x, -y, -z+1; xvii = -x+1, -y, -z+1).

**Table S2.** Selected parameters for the  $\pi$ - $\pi$  stacking study.

Compound	i	j	DC	ANG	DZ	DXY	DS	DZ'	DXY'	DS'
<b>1</b>	1	3 <sup>i</sup>	3.46	1.82	3.27	1.13	3.48	3.30	1.16	–
	2	2 <sup>i</sup>	3.33	0.00	3.27	0.76	3.62	3.27	0.76	3.62
	3	1 <sup>i</sup>	3.46	1.82	3.30	1.16	–	3.27	1.13	3.48
<b>2</b>	2	4	3.66	4.86	3.24	1.70	3.99	3.14	1.67	–
	3	4	3.26	1.84	3.21	0.74	–	3.20	0.65	–
<b>3</b>	1	1 <sup>ii</sup>	3.87	1.19	3.56	1.14	3.73	3.56	1.12	3.73
	2	3 <sup>iii</sup>	3.68	9.19	3.52	1.54	4.33	3.32	1.64	–
	3	3 <sup>iii</sup>	3.56	1.90	3.50	0.78	–	3.50	1.09	–
	5	5 <sup>iv</sup>	4.06	0.00	3.77	1.69	3.97	3.77	1.69	3.97
<b>4</b>	6	6 <sup>v</sup>	3.75	0.00	3.30	1.75	3.45	3.30	1.75	3.45
<b>5</b>	6	6 <sup>vi</sup>	3.75	0.00	3.33	1.75	3.45	3.33	1.75	3.45

(i =  $-x+2, -y+1, -z+1$ ; ii =  $-x, y, -z+1/2$ ; iii =  $-x+1, y, -z+1/2$ ; iv =  $-x+1/2, -y+1/2, -z$ ; v =  $-x+1, -y+1, -z$ ; vi =  $-x+1, -y, -z$ ).

1: Pyridinic ring. Considered atoms: N1, C1, C2, C3, C4 and C5.

2: Chelating ring. Considered atoms: Cu1, N1, C5, C6 and N2.

3: Chelating ring. Considered atoms: Cu1, N2, N3, C7 y S1.

4: Chelating ring. Considered atoms: Cu2, N5, C12, C13 y O1.

5: Pyridinic ring. Considered atoms: N5, C8, C9, C10, C11 y C12.

6: Pyridinic ring. Considered atoms: N11, C11, C21, C31, C41 y C51.

DC: Distance (Å) between centroids of i and j fragments.

ANG: Angle ( $^{\circ}$ ) between least squares planes.

DZ: Distance (Å) between the centroid of j fragment and the least squares plane of i.

DZ': Distance (Å) between the centroid of i fragment and the least squares plane of j.

DXY: Distance (Å) between centroids of i and j projected over the least squares plane of i.

DXY': Distance (Å) between centroids of i and j projected over the least squares plane of j.

DS: Distance (Å) between the centroid of j and nearest hydrogen atom of i.

DS': Distance (Å) between the centroid of i and nearest hydrogen atom of j.



**Table S3.** Selected parameters for the anion- $\pi$  study.

Compound	k	l	DC	Dkl
<b>4</b>	O12	1 <sup>i</sup>	3.29	O12...Cu2: 2.86; O12...N22: 3.12
	O12	2 <sup>i</sup>	2.89	O12...Cu2: 2.86; O12...N22: 3.12
	O22	1 <sup>i</sup>	3.59	O22...N22: 3.22; O22...N32: 3.32
	O22	2 <sup>i</sup>	3.59	O22...N22: 3.22; O22...C62: 3.32
	O32	2 <sup>i</sup>	3.51	O32...C52: 3.28; O32...C62: 3.40
	O32	3 <sup>i</sup>	3.76	O32...C52: 3.28; O32...C42: 3.55
<b>5</b>	O12	1	3.32	O12...Cu2: 2.89; O12...N22: 3.12
	O12	2	2.89	O12...Cu2: 2.89; O12...N22: 3.12
	O22	1	3.59	O22...N22: 3.23; O22...N32: 3.32
	O22	2	3.61	O22...N22: 3.23; O22...C62: 3.34
	O32	2	3.50	O32...C52: 3.29; O32...C62: 3.39
	O32	3	3.76	O32...C52: 3.29; O32...C42: 3.55

(i = x-1, y, z).

1: Chelating ring. Considered atoms: Cu2, N22, N32, C72 and S2.

2: Chelating ring. Considered atoms: Cu2, N12, C52, C62 and N22.

3: Pyridinic ring. Considered atoms: N12, C12, C22, C32, C42 and C52.

DC: Distance (Å) between the oxygen atom of the nitrate anion k and the centroid of l.

Dkl: Distance (Å) between the oxygen atom of the nitrate anion k and nearest atoms of l.

**Table S4.** Most important peaks of ESI mass spectra of CuL(NO<sub>3</sub>) aqueous solutions at different pH values after 1 hour.

Without any adjustment	pH values				Assigned species	Num. Cu <sup>[a]</sup>
	7.4	9.0	11.0	13.0		
		128.8	128.8	128.9		0
		135.9	135.9	136.0		0
			142.8	142.8		0
				222.8		0
<b>241.8</b>	241.8				[CuL] <sup>+</sup>	1
		244.9				0
			262.8	262.8		0
	281.8	<b>281.8</b>	<b>281.8</b>	<b>281.8</b>		1
306.1						0
	347.8					2
	393.2	393.2	393.2	393.2		0
405.9	405.9					1
		413.1	413.1	413.1		0
463.8						1
500.8	<b>500.8</b>	500.8			[Cu <sub>2</sub> L <sub>2</sub> (OH)] <sup>+</sup>	2
	522.7	522.7	524.7	522.7		2 ó 3
528.7						2
	530.7					3
544.7	542.7	542.6	544.6	544.6		2 ó 3
558.7						2
	566.7					2
	646.7					2
	787.6					3

[a] Expected number of Cu atoms in terms of their isotopic distribution.

**Table S5.** Most important peaks of ESI mass spectra of  $[\{\text{Cu}(\text{L}')(\text{NO}_3)\}_2]$  aqueous solutions at different pH values after 1 hour.

Without any adjustment	pH values				Assigned species	Num. Cu <sup>[a]</sup>
	7.4	9.0	11.0	13.0		
				142.8		0
255.8					$[\text{Cu}(\text{L}')^+]$	1
			262.8	262.8		0
	295.8	295.8	295.8	295.8		1
393.1	393.2	393.2	393.2	393.2		0
		413.2	413.2	413.2		0
	528.9		528.8		$[\text{Cu}_2(\text{L}')_2(\text{OH})_2]^+$	2
	<b>552.7</b>	<b>550.7</b>	<b>550.7</b>	<b>550.7</b>		2 ó 3
569.8	570.7	570.7	570.6	570.7		3
	785.7					3
	807.6	807.8	807.6	807.6		3 ó 4
		1044.6	1044.6	1044.6		3 ó 4

[a] Expected number of Cu atoms in terms of their isotopic distribution.

**Table S6.** Most important peaks of ESI mass spectra of  $\text{FeL}_2(\text{NO}_3)(\text{H}_2\text{O})$  aqueous solution without any pH adjustment after 1 hour.

Without pH adjustment	Assigned species
193.9	
211.9	
222.8	
234.9	$[\text{FeL}]^+$
250.9	
<b>267.8</b>	
284.8	
308.9	
337.9	
355.9	
371.8	
413.8	$[\text{FeL}_2]^+$

**Table S7.** Aqua ions standard reduction potentials (pH = 0, T = 25 °C and P = 1 atm) compared to the limit values for the water stability field.<sup>1</sup>

Reaction	E° (mV)
$\text{Cu}^{2+} + \text{e}^{-} \rightleftharpoons \text{Cu}^{+}$	153
$\text{Fe}^{3+} + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}$	771
$\text{Pb}^{2+} + 2 \text{e}^{-} \rightleftharpoons \text{Pb}$	-126.2
$\text{PbO}_2 + 4 \text{H}^{+} + 2 \text{e}^{-} \rightleftharpoons \text{Pb}^{2+} + 2 \text{H}_2\text{O}$	1455
$\text{Zn}^{2+} + 2 \text{e}^{-} \rightleftharpoons \text{Zn}$	-761.8
$\text{Co}^{3+} + \text{e}^{-} \rightleftharpoons \text{Co}^{2+}$	1920
$2 \text{H}^{+} + 2 \text{e}^{-} \rightleftharpoons \text{H}_2$	0
$\text{O}_2 + 4 \text{H}^{+} + 4 \text{e}^{-} \rightleftharpoons 2 \text{H}_2\text{O}$	1229

**Table S8.** Standard reduction potentials of some thiosemicarbazonometal complexes.

Thiosemicarbazonometal entity	E° (mV)
$[\text{CuL}]^{+} \rightleftharpoons [ \{ \text{CuL}(\text{CH}_3\text{COO}) \}_2 ]$	$-150 \pm 20, ^2 \pm 2^3$
$[\text{Cu}(\text{L}') ]^{+} \rightleftharpoons [ \{ \text{Cu}(\text{L}')(\text{CH}_3\text{COO}) \}_2 ]$	$-260 \pm 20^2$
$[\text{FeL}_2]^{+}$	$242^4$
$[\text{FeL}_2](\text{NO}_3)$	$0.15 \pm 0.01^5$

<sup>1</sup> W. M. M. Haynes, *CRC Handbook of Chemistry and Physics*, Taylor and Francis Group, 92<sup>nd</sup> edn Internet Version, 2012.

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